REMARKS

Claims 1-75 are pending in this application.

Applicants again note with appreciation the Examiner's indication in the Office Action that Claims 63-75 are allowed.

The Examiner has rejected Claims 1-11, 13-37, 39-51 and 53-62 under 35 U.S.C. §112, first paragraph, because the specification, while being enabling for the disclosed derivatives, does not reasonably provide enablement for all of the derivatives encompassed by the instant claims. It is the Examiner's belief that the term "derivatives" encompasses all possible derivatives. The Examiner goes on to state that the term "derivatives" reads on an infinite number of compounds resulting from the potentially infinite number of derivations which can be performed on the recited compounds. Specifically, the Examiner relies on In re Wands (MPEP 2164.01(1)) in making the rejection by stating:

> "It is noted that the instant claims read on all potential derivations of the recited compounds which encompasses an infinite number of compounds (Wands factor A). The specification does not describe how to make all such derivatives from the infinite list thereof which will function as required in the instant invention (Wands factors F, G). It would require an infinite amount of experimentation to determine how to make all of the derivatives encompassed by the instant claims and another infinite amount of experimentation to determine which of these derivatives would function in the instantly claimed invention as required (Wands factor H). Chemistry is an unpredictable art (Wands factor E). The ordinary skilled artisan has not imagined nor figured out how to make all of the derivatives encompassed by the instant claim of "derivatives" yet (Wands factors C, D, E, F, G, and H). The enabling disclosure is not commensurate with the full scope of the claimed 'derivatives'".

Applicants respectfully disagree with the Examiner that the term "derivatives" reads on an infinite number of compounds resulting from the potentially infinite number of derivations which can be performed on the recited compounds. In contrast, the claims recite "non-nitrogen

containing derivatives of *a polyalkylene succinic anhydride*". Thus, the derivative must necessarily be a "non-nitrogen containing" derivative and the "non-nitrogen containing derivative" must be of "*a polyalkylene succinic anhydride*". One skilled in the art of chemistry and lubricant additives would readily understand what is meant by the term "non-nitrogen containing derivatives of a polyalkylene succinic anhydride".

In addition, it is well established that the specification must provide sufficient teaching such that one skilled in the art could make and use the full scope of the invention without undue experimentation. *Warner-Lambert Co. v. Teva Pharmaceuticals USA Inc.*, 75 USPQ2d 1865, 1872, 418 F3d 1326 (Fed. Cir. 2005). However, the key word is "undue" and not "experimentation". *Wands*, 858 F.2d at 737. Thus, the specification need only teach those aspects of the invention that one skilled in the art could *not* figure out without undue experimentation. See, e.g., *Nat'l Recovery Techs., Inc. v. Magnetic Separation Sys., Inc.*, 166 F.3d 1190, 1196, 49 USPQ2d 1671 (Fed. Cir. 1999) ("The scope of enablement ... is that which is disclosed in the specification plus the scope of what would be known to one of ordinary skill in the art without undue experimentation.").

Applicants submit that the specification clearly teaches the recitation "non-nitrogen containing derivatives of *a polyalkylene succinic anhydride*" as presently recited in Claims 1, 18 and 43 such that one skilled in the art could make and use the "non-nitrogen containing derivatives of *a polyalkylene succinic anhydride*" without undue experimentation. First, the specification discloses the term "polyalkylene succinic anhydride" at page 11, lines 1-5:

> "The polyalkylene succinic anhydride dispersing agent is preferably a polyisobutenyl succinic anhydride (PIBSA). The number average molecular weight of the polyalkylene tail in the polyalkylene succinic anhydrides used herein will be at least 350, preferably from about to about 750 to about 3000 and most preferably from about 900 to about 1100."

Second, the specification sets forth in the paragraph bridging pages 11 and 12 how a "polyalkylene succinic anhydride" is obtained. Finally, the specification sets forth on page 12, lines 15-19 examples of "non-nitrogen containing derivatives of a polyalkylene succinic anhydride", i.e., succinic acids, Group I and/or Group II mono- or di-metal salts of succinic acids, succinate esters formed by the reaction of a polyalkylene succinic anhydride, acid chloride, or other derivatives with an alcohol (e.g., HOR^1 wherein R^1 is an alkyl group of from 1 to 10 carbon atoms).

Further, Applicants submit that the term "non-nitrogen containing derivatives of a polyalkylene succinic anhydride" is clearly within the scope of what would be known to one of ordinary skill in the art of chemistry and specifically lubricant additives without undue experimentation. Non-nitrogen containing derivatives of a polyalkylene succinic anhydride are well known lubricant dispersants. This is illustrated in, for example, Lubricant Additives, Chemistry and Applications, Leslie R. Rudnick (editor), Marcel Dekkar, Inc., pp. 150-155 (2003) (Exhibit 1) which shows dispersants obtained from the reaction of a polyalkylene succinic anhydride with an alcohol in Figure 12. This is further illustrated in, for example, U.S. Patent No. 6,632,781 (Exhibit 2) and U.S. Patent Application Publication No. 20020147115 (Exhibit 3). Accordingly, the claimed "non-nitrogen containing derivatives of a polyalkylene succinic anhydride" are believed to be fully enabled such that one skilled in the art of chemistry and lubricant additives could figure out how to make these compounds without undue

experimentation. Such being the case, the recitation "non-nitrogen containing derivatives of a polyalkylene succinic anhydride" as presently recited in Claims 1, 18 and 43 is believed to comply with the requirement for the first paragraph of 35 U.S.C. §112. Therefore, withdrawal of the rejection of Claims 1-11, 13-37, 39-51 and 53-62 under 35 U.S.C. §112, first paragraph, is respectfully requested.

The Examiner has rejected Claims 1-11, 14-23, 26-37, 39-40, 42-45, 48-51 and 54-62 under 35 U.S.C. §103(a) as being obvious over Price U.S. Patent No. 3,140,997 ("Price") in view of Valcho et al. U.S. Patent No. 4,601,837 ("Valcho et al."). This rejection is respectfully traversed.

Nowhere does Price disclose or suggest a stable colloidal suspension comprising "(a) a dispersed phase comprising a major amount of one or more dispersed hydrated polymeric compounds selected from ... polymolybdates ... and, (b) an oil phase comprising one or more dispersing agents selected from the group consisting of polyalkylene succinic anhydrides, non-nitrogen containing derivatives of a polyalkylene succinic anhydride and mixtures thereof and a diluent oil, wherein the stable colloidal suspension is substantially clear" as presently recited in independent Claim 1.

Likewise, nowhere does Price disclose or suggest a process for preparing a stable colloidal suspension comprising:

"mixing, under agitation, (a) an aqueous solution comprising one or more hydrated polymeric compounds selected from the group consisting of polymolybdates ...; (b) one or more dispersing agents selected from the group consisting of polyalkylene succinic anhydrides, non-

nitrogen containing derivatives of a polyalkylene succinic anhydride and mixtures thereof and (c) a diluent oil to form a micro emulsion; and,

heating the micro emulsion to a temperature to remove sufficient water so as to produce a stable colloidal suspension comprising (a) a dispersed phase comprising a major amount of one or more dispersed hydrated polymeric compounds selected from … polymolybdates … and, (b) an oil phase comprising one or more dispersing agents selected from the group consisting of polyalkylene succinic anhydrides, non-nitrogen containing derivatives of a polyalkylene succinic anhydride and mixtures thereof and a diluent oil, wherein the stable colloidal suspension is substantially clear" as presently recited in independent Claim 18.

Nor does Price disclose or suggest a process for preparing a stable colloidal suspension comprising:

"mixing, under agitation, an (a) aqueous solution comprising (i) one or more monomeric compounds selected from the group consisting of molybdenum … and (ii) an effective amount of an acid capable of at least partially polymerizing the one or more monomeric compounds; (b) one or more dispersing agents selected from the group consisting of polyalkylene succinic anhydrides, non-nitrogen containing derivatives of a polyalkylene succinic anhydride and mixtures thereof and (c) a diluent oil to form a micro emulsion; and,

heating the micro emulsion to a temperature to remove sufficient water so as to produce a stable colloidal suspension comprising (a) a dispersed phase comprising a major amount of one or more dispersed hydrated polymeric compounds selected from … polymolybdates … and, (b) an oil phase comprising one or more dispersing agents selected from the group consisting of polyalkylene succinic anhydrides, non-nitrogen containing derivatives of a polyalkylene succinic

anhydride and mixtures thereof and a diluent oil, wherein the stable colloidal suspension is substantially clear" as presently recited in independent Claim 43.

In order to establish a *prima facie* case of obviousness, the Examiner maintains in the Office Action:

> "It would have been obvious to one of ordinary skill in the art at the time of the instantly claimed invention to use the instantly claimed combinations and ingredients and amounts thereof and the methods of making the instantly claimed compositions because they are encompassed by the patentee and would have been expected to give the benefits disclosed by the patentee. ... It would have been obvious to one of ordinary skill in the art at the time of the instantly claimed invention to use the instantly claimed polyalkylene succinic anhydrides as the dispersants of Price because Valcho et al. shows such dispersants to improve the efficiency of molybdenum incorporation into similar dispersions and to improve product clarity at column 2, lines 31-37 and these improvements would have been expected in the compositions of Price."

It is the Applicant's view that the Examiner's reasoning that it would be obvious to use the claimed polyalkylene succinic anhydrides dispersants in the dispersion of Price is misplaced. Price discloses that the dispersants used in the practice of his invention "should have sufficient *alkalinity* and should be used in a sufficient quantity to *neutralize* the free acid in the ketone extract." Price further discloses that "[t]he ratio of dispersant to molybdenum will depend largely on the basicity of the dispersant." Thus, the dispersants disclosed in Price must be an *alkaline* dispersant to *neutralize* the free acid in the ketone extract. In contrast, the recited dispersing agents selected from the group consisting of polyalkylene succinic anhydrides, non-nitrogen containing derivatives of a polyalkylene succinic anhydride and mixtures are *acidic* dispersing agents, not alkaline dispersing agents as required by Price. Accordingly, the dispersants disclosed in Price are completely different than the dispersants recited in Claims 1,

18 and 43. As such, there is no reason why one skilled in the art would look to use the polyalkylene succinic anhydride dispersants disclosed Valcho et al., which are acidic dispersants, to neutralize the free acid in the ketone extract disclosed in place of the alkaline dispersants disclosed in Price and arrive at the claimed invention.

The Examiner further maintains in the Office Action:

> "The applicant argues that the patentee does not disclose the instantly claimed invention as argued at page 15, lines 5-12 of their arguments. The applicant has not shown the colloidal dispersions of the patentee to not possess the instantly claimed clarity nor that the polymolybdenates of the patentee are not the major phase of the resulting colloid disperse phase nor that the dispersions are not stable. As stated above, it appears that the components and processing are the same as those of the instant claims and would have been expected to yield the instantly claimed clear dispersion, as indicated by 'colloid'. The applicant provides no probative evidence to the contrary. The applicant argues regarding "Molybdenum: The Element and Aqueous Solution Chemistry, vol. 36.1, pp. 1256-1264. This contradicts the reference cited below. Thus, the examiner cannot tell which reference is correct. There is no probative evidence that the prior art low pH compositions do not form the polymeric molybdenates. Furthermore, it is not seen that the dimer is not polymeric either. ... It is further not seen via probative evidence that the method of example 2 of the patentee that gives a colloidal dispersion does remove too much water, according to the instant invention, does not contain polymeric molybdenate, and is not clear. The reference resubmitted, "Molybdenum Compounds", Vol. 16, page 941, states that below pH of 7 the polymeric forms of the molybdenates exist."

Applicants respectfully request clarification. The reference, Molybdenum Compounds, Vol. 16, page 941 (Exhibit 4), states that below pH of 7 the polymeric forms of the molybdenates exist. The other reference, Molybdenum: The Element and Aqueous Solution Chemistry, Volume 36.1, pp. 1256-1264 (Exhibit 5), states that "The incidence of protonation at pH ~ 7 triggers polymerization. Polymeric forms play a dominant role in the chemistry of Mo^{VI} from pH 7 down to 2." Certainly, these statements do not contradict each other. In fact, the reference,

Molybdenum: The Element and Aqueous Solution Chemistry, Volume 36.1, pp. 1256-1264 (Exhibit 5), clarifies that "[a]t pH 2 to 1 (depending on the concentration) breakdown of polymers to give dimeric and monomeric octahedral forms occurs, where the latter are often referred to as $[Mo(OH)_6]$."

Price discloses that sufficient mineral acid such as HCl is added to a molybdenum compound to furnish a solution having a normality of 2 to 12 and preferably 4 to 8. One skilled in the art of chemistry would readily understand that the pH of a solution having a normality of 2 to 12 would be less than 2. The reference, Molybdenum: The Element and Aqueous Solution Chemistry, Volume 36.1, pp. 1256-1264, further clarifies that "[a]t pH 2 to 1 (depending on the concentration) breakdown of polymers to give dimeric and monomeric octahedral forms occurs, where the latter are often referred to as $[Mo(OH)_6]$." Any polymeric form of a molybdate that may be present would therefore necessarily breakdown and no longer be in its polymeric form. As such, a dimeric form would necessarily have to be *different* than a polymeric form. Accordingly, one skilled in the art would not even arrive at the claimed invention by combining Valcho et al. with Price. Thus, as stated above, there is no reason why one skilled in the art would look to use the polyalkylene succinic anhydride dispersants disclosed Valcho et al. in forming the colloidal molybdenum complex disclosed in Price, which uses alkaline dispersants and arrive at the claimed invention.

For the foregoing reasons, one skilled in the art would not look to combine Price with Valcho et al. As such, Claims 1-11, 14-23, 26-37, 39-40, 42-45, 48-51 and 54-62 are believed to be nonobvious, and therefore patentable over the combination of Price with Valcho et al., no matter how these references are considered or combined. Accordingly, withdrawal of the

rejection of Claims 1-11, 14-23, 26-37, 39-40, 42-45, 48-51 and 54-62 under 35 U.S.C. §103(a) is respectfully requested.

For the foregoing reasons, Claims 1-11, 13-23, 25-37, 39-51 and 53-75 as presented herein are believed to be in condition for allowance. Such early and favorable action is earnestly solicited.

Respectfully submitted,

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Enclosures
Exhibit 1: Lubricant Additives, Chemistry and Applications, Leslie R. Rudnick (editor), Marcel Dekkar, Inc., pp. 150-155 (2003)
Exhibit 2: U.S. Patent No. 6,632,781
Exhibit 3: U.S. Patent Application Publication No. 20020147115
Exhibit 4: Molybdenum Compounds, Vol. 16, page 941 (1995)
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LUBRICANT ADDITIVES

CHEMISTRY AND APPLICATIONS

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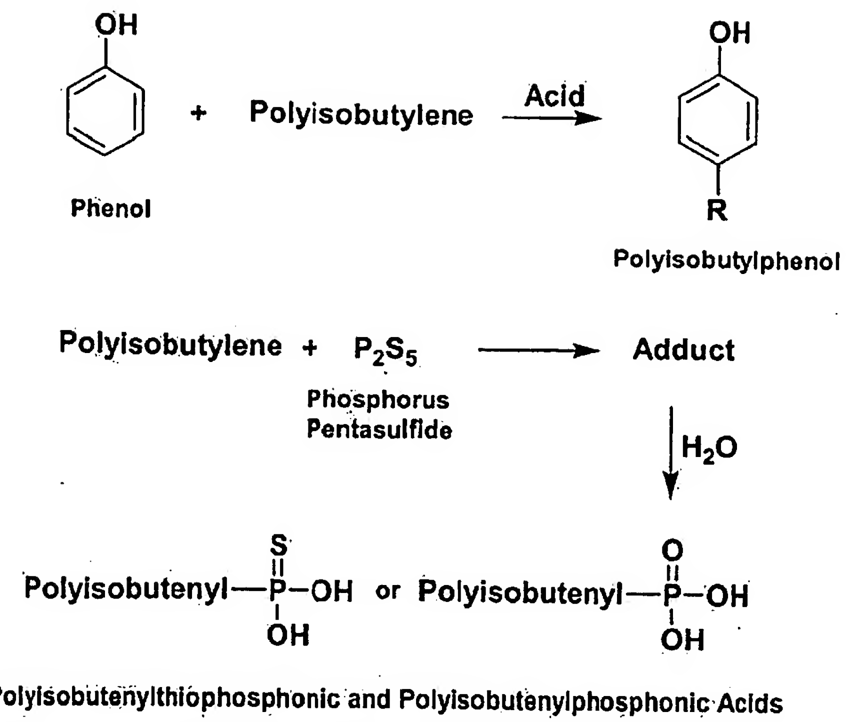


Figure 8 Synthesis of alkylphenols and alkenylphosphonic acids.

A new carboxylate moiety derived from glyoxylic acid to make dispersants has been reported in the literature [59–63]. However, at present no commercial products appear to be based on this chemistry.

6.3 The Polar Moiety

The two common polar moieties in dispersants are based on polyamines and polyhydric alcohols. The structures of common amines and alcohols used to make dispersants are shown in Figure 9.

The polyamines are manufactured from ethylene via chlorination, followed by reaction with ammonia [64]. The reaction scheme is given in Figure 10. As shown, polyamines contain piperazines as a byproduct. Examining the structures of various amines, one can see that they contain primary amino groups, secondary amino groups, and tertiary amino groups. Each type of amino group has different reactivity toward alkenylsuccinic anhydride. The primary amino group reacts with the anhydride to form a cyclic imide, the secondary amino group reacts with the anhydride to form an amide/carboxylic acid, and the tertiary amino group does not react with the anhydride at all [65].

However, it can make a salt if a free carboxylic acid functionality is present in the molecule, as is the case in amide/carboxylic acid. These reactions are shown in Figure 11. New high-molecular-weight amines derived from phosphoric acid–catalyzed condensation of polyhydroxy compounds, such as pentaerythritol, and polyalkylene-polyamines, such as triethylenetetramine, are known [66]. These amines

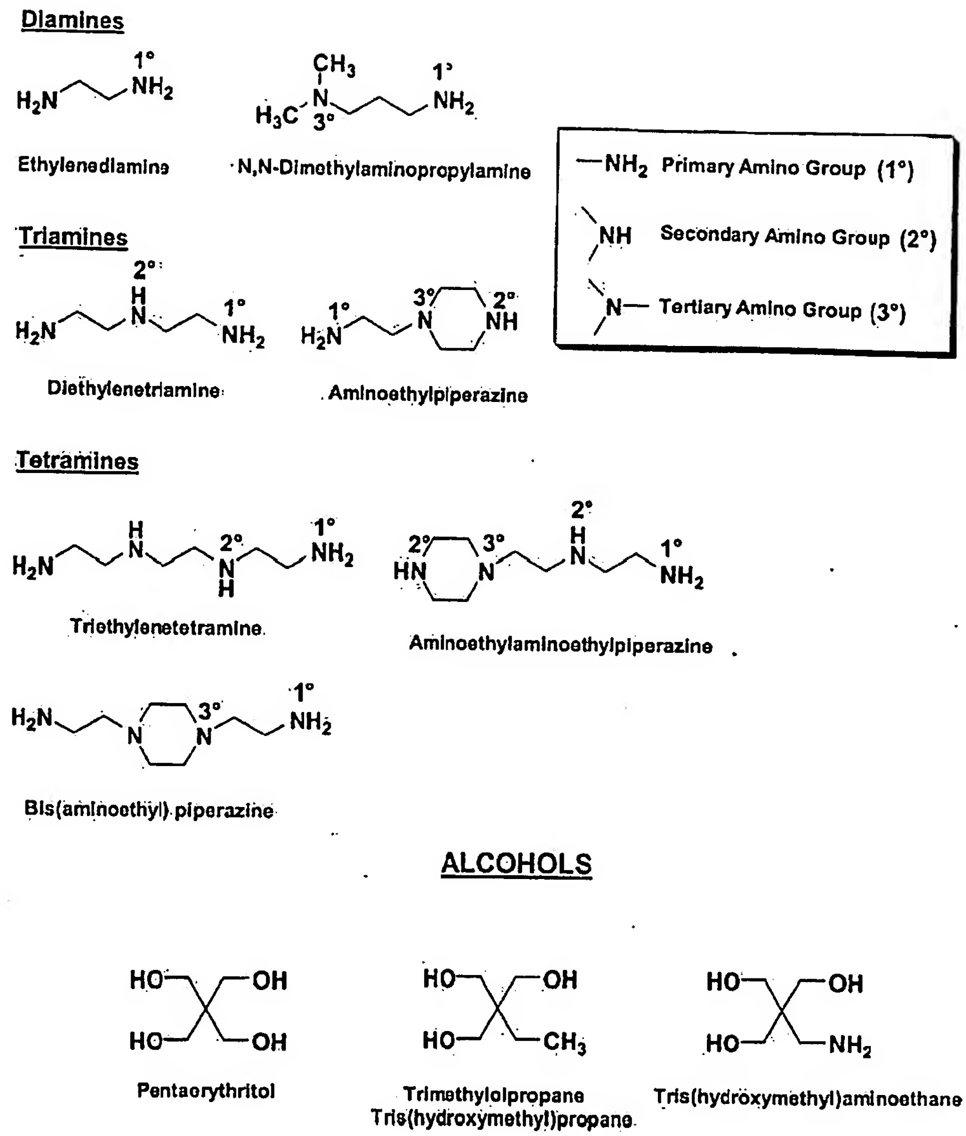


Figure 9 Amines and alcohols used to synthesize dispersants.

are claimed to form high TBN (total base number) dispersants with low free-amine content and better engine test performance than dispersants made from conventional polyamines.

Imide and ester dispersants are made by reacting polyamines and polyhydric alcohols with alkenylsuccinic anhydrides. The reaction typically requires a reaction temperature between 130°C and 200°C to remove the resulting water and complete the reaction [44]. As mentioned earlier, imide dispersants are made by the use of polyalkylene-polyamines, such as diethylenetriamine and triethylenetetramine. Many polyhydric alcohols can be used to make ester dispersants. These include trimethylolpropane, tris(hydroxymethyl)aminoethane, and pentaerythritol. When one

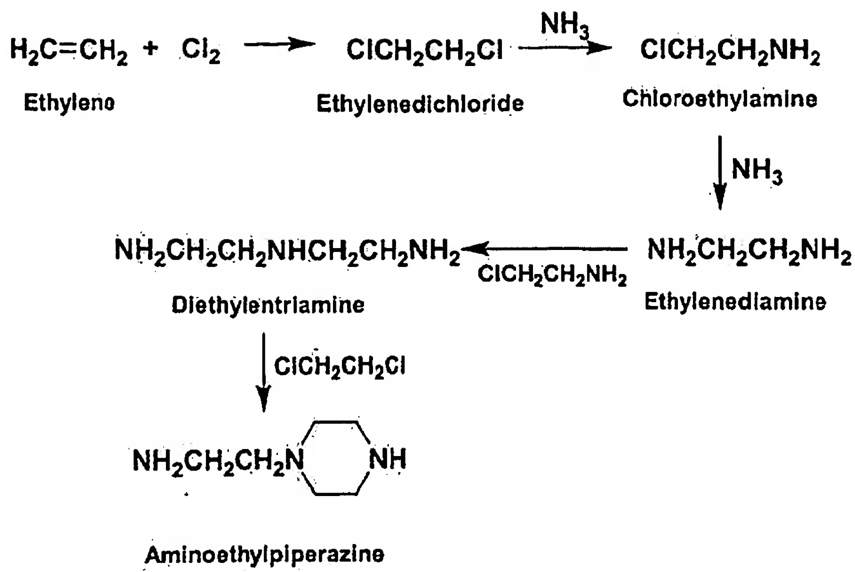


Figure 10 Manufacture of polyamines.

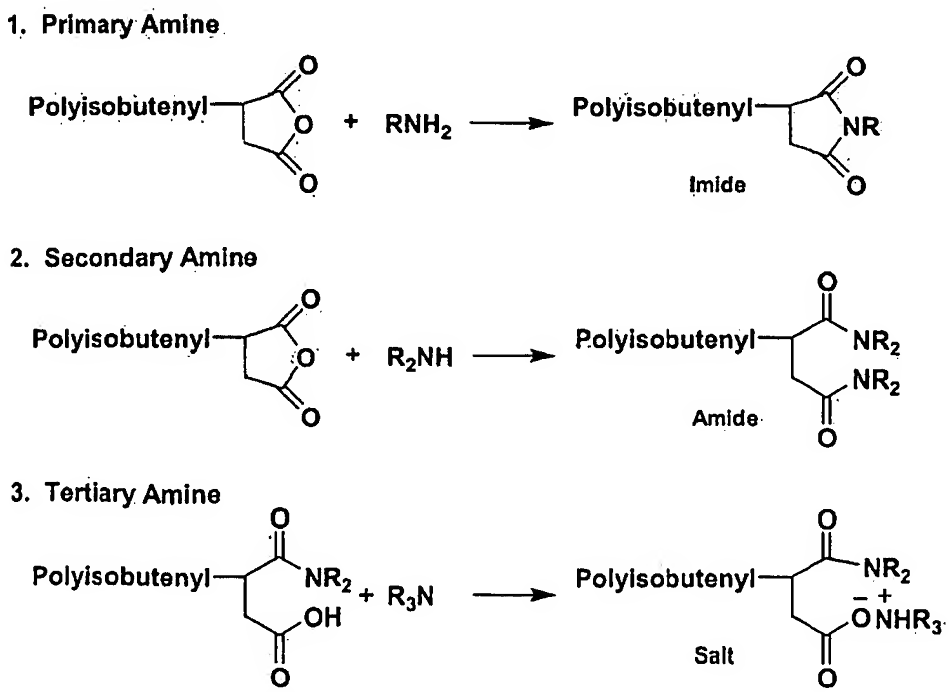
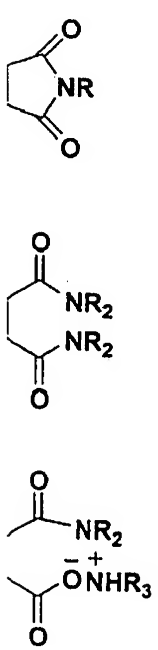


Figure 11 Amine-anhydride reaction products. (Based on Ref. 53.)

IH2
ine
2NH2
iine



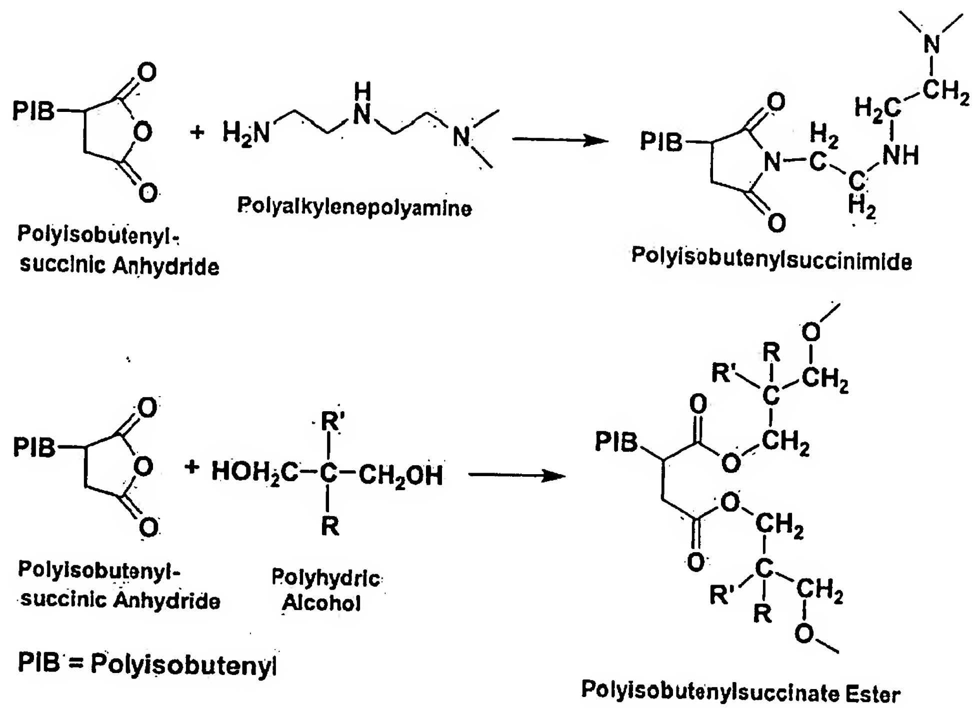


Figure 12 Synthesis of imide and ester dispersants.

uses tris(hydroxymethyl)aminoethane as the alcohol, one can obtain an ester dispersant with basicity. The reaction schemes to make succinimide and succinate dispersants are depicted in Figure 12.

The alkylphenol-derived dispersants are made by reacting an alkylphenol, such as polyisobutylphenol, with formaldehyde and a polyamine [56,67]. The result is the formation of 2-aminomethyl-4-polyisobutylphenol. The reaction of ammonia or an amine, formaldehyde, and a compound with active hydrogen(s), such as a phenol, is called the *Mannich reaction* [68,69]. Hence, such dispersants are called Mannich dispersants. For making phosphonate dispersants, the common method is to react the free acid with an olefin epoxide, such as propylene oxide or butylene oxide, or an amine [2,70,71]. These reactions are summarized in Figure 13. Salts derived from the direct reaction of amine and metal bases with olefin-phosphorus pentasulfide adduct are also known [72,73]. It is important to note that structures in figures are idealized structures. The actual structures will depend on the substrate- (alkylphenol and alkenylsuccinic anhydride) to-reactant (formaldehyde and polyamines) ratio.

Because of the polyfunctionality of the succinic anhydride group and of the amines and the polyhydric alcohols, a variety of dispersants can be made by altering the anhydride-to-amine or anhydride-to-alcohol ratios. These dispersants differ not only in their molecular weight but also in their properties. Polyfunctionality of the two reactants leads to dispersants, which have molecular weights that are 3 to 7 times higher than expected if the two reactants were monofunctional.

The methods to make dispersant viscosity modifiers are shown in Figures 14 to 16. These are synthesized by:

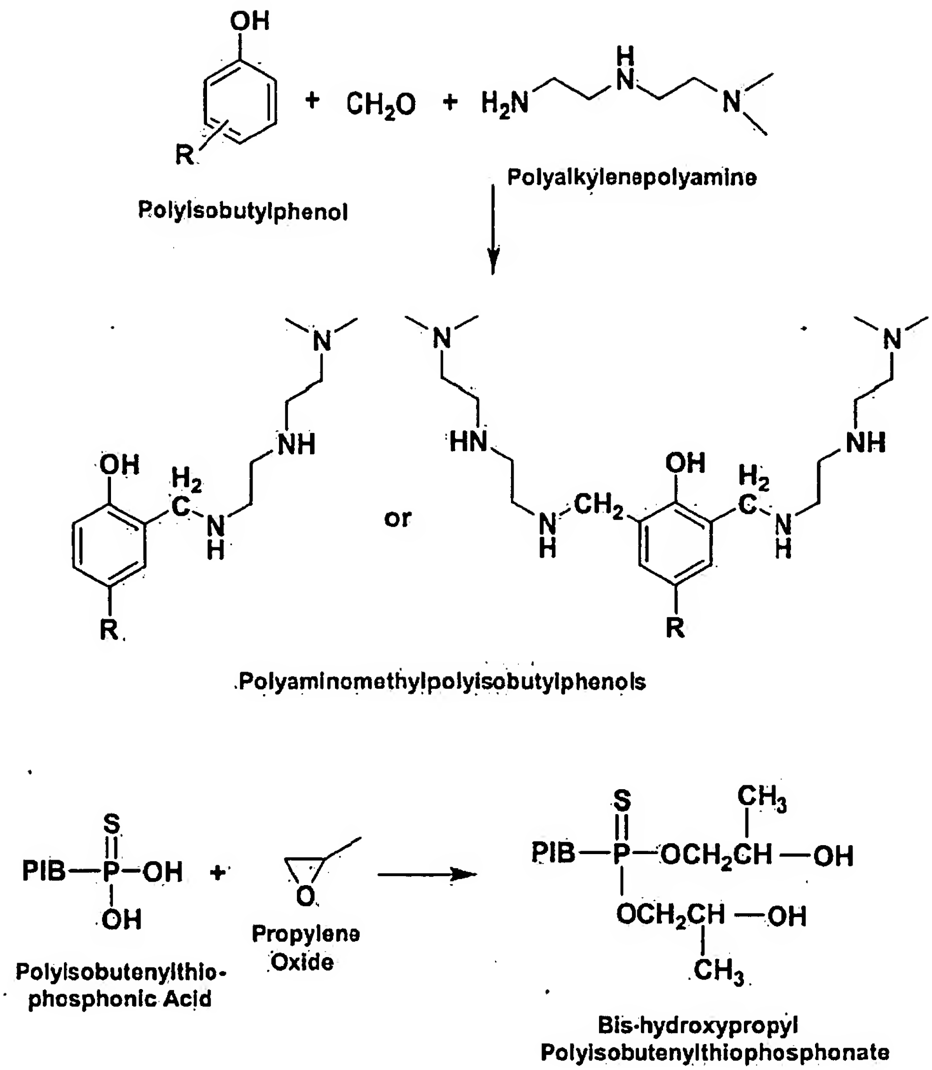


Figure 13 Synthesis of Mannich and phosphonate dispersants.

- Grafting or reacting of a dispersancy-imparting monomer on an already-formed polymer, as in the case of EPRs and SDRs [74–82]
- Including such a monomer during the polymerization process, as in the case of polyacrylates and polymethacrylates [83]
- Introducing a reactive functional group in the polymer that can be reacted with a reagent to impart dispersancy, as in the case of styrene-maleic anhydride copolymers [86–94]

While most of the examples in the figures pertain to introduction of the basic nitrogen-containing moieties, neutral dispersant viscosity modifiers are also known in the literature. These are made by using nonbasic reactants, such as *N*-vinylpyrrolidinone, alcohols, or polyether-derived methacrylate ester [77,84,95]. Recently,

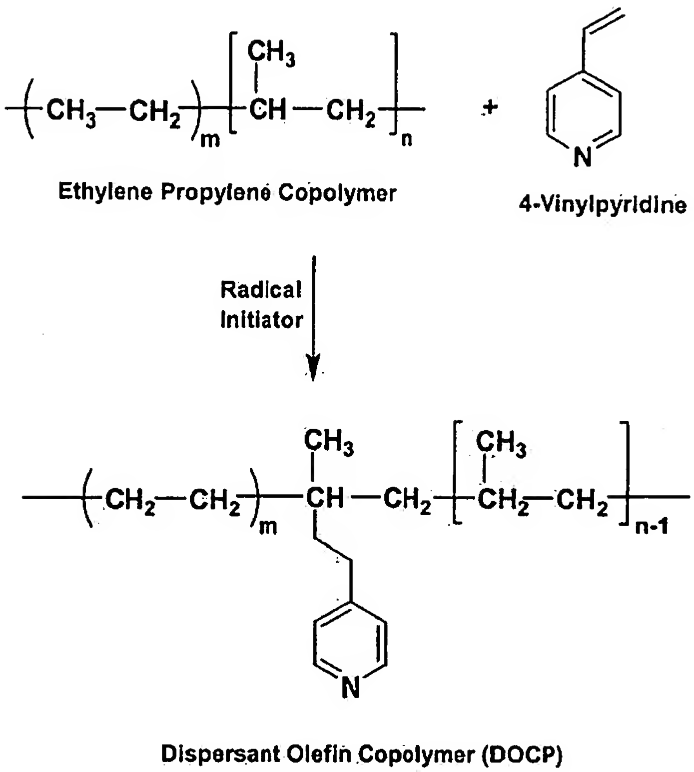


Figure 14 Dispersant viscosity modifier synthesis via grafting.

dispersant viscosity-improving additives with built-in oxidation inhibiting and antiwear moieties have been reported in the patent literature [75,96,97]. Dispersant polymers containing oxidation-inhibiting moieties are commercially available from Texaco Chemical Company now part of Ethyl Petroleum Additives Company. As the examples show, grafting usually allows the introduction of the connecting group in the dispersant polymers at the same time as the polar moiety.

7 DISPERSANT PROPERTIES

A dispersant consists of a hydrocarbon chain, a connecting group, and a polar functionally. While each structural feature imparts unique properties to a dispersant, the dispersant's overall performance depends on all three. The overall performance is assessed in terms of its dispersancy, thermal and oxidative stability, viscosity characteristics, and seal performance. These criteria primarily relate to engine oils, where dispersants find major use.

7.1 Dispersancy

As mentioned, dispersancy pertains to a dispersant's ability to suspend byproducts of combustion, such as soot, and lubricant degradation, such as resin, varnish, lacquer, and carbon deposits. The overall performance of a dispersant depends on all

US006632781B2

(12) United States Patent
Harrison et al.

(10) Patent No.: US 6,632,781 B2
(45) Date of Patent: *Oct. 14, 2003

(54) LUBRICANT COMPOSITION COMPRISING ALKALI METAL BORATE DISPERSED IN A POLYALKYLENE SUCCINIC ANHYDRIDE AND A METAL SALT OF A POLYISOBUTENYL SULFONATE

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(73) Assignee: **Chevron Oronite Company LLC**, San Ramon, CA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **09/967,049**

(22) Filed: **Sep. 28, 2001**

(65) **Prior Publication Data**

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(51) **Int. Cl.**^{7} **C01M 125/26**; C01M 141/08
(52) **U.S. Cl.** **508/158**; 508/156; 508/306; 508/390; 508/413
(58) **Field of Search** 508/156, 158, 508/306, 390

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Primary Examiner—Ellen M. McAvoy
(74) *Attorney, Agent, or Firm*—Joseph P. Foley; Claude J. Caroli

(57) **ABSTRACT**

Disclosed are lubricant compositions comprising a dispersed hydrated alkali metal borate, a polyalkylene succinic dispersant selected from a polyalkylene succinic anhydride, a mixture of polyalkylene succinic anhydrides or derivatives thereof; and a metal salt of a polyisobutenyl sulfonate. Also disclosed are methods for improving the water tolerance of a lubricant composition and methods for preparing such lubricants comprising a dispersed hydrated alkali metal borate and a dispersant mixture.

19 Claims, No Drawings

LUBRICANT COMPOSITION COMPRISING ALKALI METAL BORATE DISPERSED IN A POLYALKYLENE SUCCINIC ANHYDRIDE AND A METAL SALT OF A POLYISOBUTENYL SULFONATE

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

This invention is directed, in part, to novel lubricant compositions. These compositions comprise an alkali metal borate; a polyalkylene succinic anhydride including mixtures and/or derivatives thereof; and a metal salt of a polyisobutenyl sulfonate. Surprisingly, these compositions have improved compatibility, extreme pressure properties and/or water tolerance over compositions comprising other metal sulfonates.

This invention is also directed, in part, to methods for improving the water tolerance of a lubricant composition comprising an alkali metal borate. Such methods employ compositions comprising an alkali metal borate; and a polyalkylene succinic anhydride including mixtures and/or derivatives thereof; and a metal salt of a polyisobutenyl sulfonate.

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[7] Adams, U.S. Pat. No. 4,163,729, Synergistic Combinations of Hydrated Potassium Borate, Antiwear Agents, and Organic Sulfide Antioxidants, issued Aug. 7, 1979

[8] Frost, U.S. Pat. No. 4,263,155, Lubricant Composition Containing an Alkali Metal Borate and a Sulfur-Containing Polyhydroxy Compound, U.S. Pat. No. 5,461,184, issued Oct. 24, 1995

[9] Frost, U.S. Pat. No. 4,401,580, Lubricant Composition Containing an Alkali Metal Borate and an Ester-Polyol Compound, issued Aug. 30, 1983

[10] Frost, U.S. Pat. No. 4,472,288, Lubricant Composition Containing an Alkali Metal Borate and an Oil-Soluble Amine Salt of a Phosphorus Compound, issued Sep. 18, 1984

[11] Clark, U.S. Pat. No. 4,584,873, Automotive Friction Reducing Composition, issued Aug. 13, 1985

[12] Brewster, U.S. Pat. No. 3,489,619, Heat Transfer and Quench Oil, issued Jan. 13, 1970

All of the above references are herein incorporated by reference in their entirety to the same extent as if each individual publication or patent was specifically and individually indicated to be incorporated by reference in its entirety.

STATE OF THE ART

High load conditions often occur in gear sets such as those used in automobile transmissions and differentials, pneumatic tools, gas compressors, centrifuges, high-pressure hydraulic systems, metal workings and similar devices as well as in many types of bearings. When employed in such environments, it is conventional to add an extreme-pressure agent to the lubricant composition and, in this regard, alkali metal borates are well known extreme-pressure agents for such compositions.[1-12]

Because the alkali metal borate is insoluble in lubricant oil media, it is conventional to include a dispersant/detergent in such compositions in order to facilitate the formation of a homogenous dispersion. Examples of dispersant/detergents include ionic surface-active agents such as metal salts of oil soluble acidic organic compounds, e.g., sulfonates, carboxylates and phenolates, as well as non-ionic surface-active agents such as alkenyl succinimides or other nitrogen containing dispersants.[1-4] It is also conventional to employ the alkali metal borate at particle sizes of less than 1 micron in order to facilitate the formation of the homogenous dispersion.[11]

The use of alkali metal borates in lubricant compositions is complicated by the presence of water in the environment where the composition is employed. Conventional preparation methods remove essentially all the water from the media[12]. However, when the presence of water exceeds a threshold concentration in the lubricant composition, the borate crystallizes out of the composition and forms hard granules. These granules cause severe noise in the lubricated systems and can severely damage the gears or bearings themselves as well as leading to seal leakage.[10] Further, borate lost by crystallization decreases the extreme pressure properties of the lubricant composition.

On the other hand, lubricant compositions employing alkali metal borates are often employed in environments where water is invariably present.

In view of the above, enhanced water tolerance of lubricant compositions comprising an alkali metal borate would be particularly beneficial.

SUMMARY OF THE INVENTION

This invention is directed to the novel and unexpected discovery that enhanced water tolerance and lubricant oil compatibility for alkali metal borates can be achieved by employing a dispersant mixture comprising:

a) a polyalkylene succinic dispersant which is selected from the group consisting of a polyalkylene succinic anhydride, a non-nitrogen containing derivative of the polyalkylene succinic anhydride, mixtures of polyalkylene succinic anhydrides, mixtures of non-nitrogen containing derivatives of the polyalkylene succinic anhydride and mixtures of one or more polyalkylene succinic anhydrides and one or more non-nitrogen containing derivatives of polyalkylene succinic anhydrides; and

b) a metal salt of a polyisobutenyl sulfonate.

Accordingly, in one of its composition aspects, this invention is directed to a lubricant composition which comprises a base oil of lubricating viscosity, a dispersed hydrated alkali metal borate, and a dispersant mixture comprising:

a) a polyalkylene succinic dispersant which is selected from the group consisting of a polyalkylene succinic anhydride, a non-nitrogen containing derivative of the polyalkylene succinic anhydride, mixtures of polyalky-

lene succinic anhydrides, mixtures of non-nitrogen containing derivatives of the polyalkylene succinic anhydride, and mixtures of one or more polyalkylene succinic anhydrides and one or more non-nitrogen containing derivatives of the polyalkylene succinic anhydride; and

b) a metal salt of a polyisobutenyl sulfonate.

Preferably, the dispersed hydrated alkali metal borate is present in a ratio of at least 2:1 relative to the dispersant mixture of polyalkylene succinic dispersant and polyisobutenyl sulfonate. More preferably, the ratio of dispersed hydrated alkali metal borate to dispersant mixture is from 2:1 up to 10:1. Most preferably the ratio is 5:2.

Preferably, the dispersed hydrated alkali metal borate is a dispersed hydrated sodium borate. Even more preferably the dispersed hydrated sodium borate and has a sodium to boron ratio of from about 1:2.75 to about 1:3.25.

In a particularly preferred embodiment, the dispersed hydrated alkali metal borate is a hydrated sodium metal borate having a hydroxyl:boron ratio (OH:B) of from about 0.8:1 to 1.6:1 (more preferably about 0.8:1 to 1:1) and a sodium to boron ratio of from about 1:2.75 to 1:3.25 and the polyalkylene succinic anhydride is a polyisobutenyl succinic anhydride.

Preferably, the hydrated alkali metal borate contains small amounts of a water soluble oxo anion. Only from 0.001 moles to 0.11 moles of water soluble oxo anion should be present per mole of boron. This water-soluble oxo anion can include nitrate, sulfate, carbonate, phosphate, pyrophosphate, silicate, aluminate, germanate, stannate, zincate, plumbate, titanate, molybdate, tungstate, vanadate, niobate, tantalate, uranates, or can include the isopolymolybdates and isopolytungstates, or the heteropolymolybdates and heteropolytungstates, or mixtures thereof.

Preferably, the polyalkylene succinic dispersant, is a dispersant selected from a polyalkylene succinic anhydride or a mixture of polyalkylene succinic anhydrides. More preferably, the polyalkylene succinic anhydride is a polyisobutenyl succinic anhydride. In one preferred embodiment, the polyalkylene succinic anhydride is a polyisobutenyl succinic anhydride having a number average molecular weight of at least 500, more preferably at least 900 and still more preferably from at least about 900 to about 3000.

In another preferred embodiment, a mixture of polyalkylene succinic anhydrides is employed. In this embodiment, the mixture preferably comprises a low molecular weight polyalkylene succinic anhydride component and a high molecular weight polyalkylene succinic anhydride component. More preferably, the low molecular weight component has a number average molecular weight of from about 500 to below 1000 and the high molecular weight component has a number average molecular weight of from 1000 to about 3000. Still more preferably, both the low and high molecular weight components are polyisobutenyl succinic anhydrides.

Preferably the metal salt of the polyisobutenyl sulfonate can be an alkali metal or alkaline earth metal salt. More preferably, the metal salt of the polyisobutenyl sulfonate is a calcium salt. Even more preferably, the calcium polyisobutenyl sulfonate employed has a total base number (TBN) of from about 14–17 due to the presence of some $Ca(OH)_2$ in the composition.

The polyisobutene employed is of sufficient molecular weight to provide oil-solubility to the polyisobutenyl sulfonic acid or metal salt thereof. Suitably, polyisobutenes having a number average molecular weight of from at least about 200 are employed. Preferably, the polyisobutene has a number average molecular weight of from about 200 to about 3000; more preferably, from about 300 to 2000; still more preferably, from about 400 to 1200; and even more preferably from about 500 to 1100.

This invention is also directed to methods for enhancing the water tolerance of lubricant compositions comprising alkali metal borate. Accordingly, in one of its method aspects, this invention is directed to a method for enhancing the water tolerance of lubricant compositions comprising alkali metal borate which method comprises adding an anti-wear effective amount of an alkali metal borate to a base oil of lubricating viscosity in combination with a dispersant effective amount of a dispersant mixture comprising:

a) a polyalkylene succinic dispersant which is selected from the group consisting of a polyalkylene succinic anhydride, a non-nitrogen containing derivative of the polyalkylene succinic anhydride, mixtures of polyalkylene succinic anhydrides, mixtures of non-nitrogen containing derivatives of the polyalkylene succinic anhydride, and mixtures of one or more polyalkylene succinic anhydrides and one or more non-nitrogen containing derivatives of polyalkylene succinic anhydrides; and

b) a metal salt of a polyisobutenyl sulfonate.

This invention is still further directed to methods for the preparation of such lubricant compositions. Accordingly, in another of its method aspects, this invention is directed to a method for preparing a lubricant composition comprising a base oil of lubricating viscosity, a dispersed hydrated alkali metal borate, and a dispersant mixture comprising:

a) a polyalkylene succinic dispersant which is selected from the group consisting of a polyalkylene succinic anhydride, a non-nitrogen containing derivative of the polyalkylene succinic anhydride, mixtures of polyalkylene succinic anhydrides, mixtures of non-nitrogen containing derivatives of the polyalkylene succinic anhydride, and mixtures of one or more polyalkylene succinic anhydrides and one or more non-nitrogen containing derivatives of polyalkylene succinic anhydrides; and

b) a metal salt of a polyisobutenyl sulfonate

which method comprises:

mixing, under agitation, (1) an aqueous solution of boric acid and alkali metal hydroxide, and (2) a diluent oil containing the polyalkylene succinic dispersant and the metal salt of a polyisobutenyl sulfonate; then heating the mixture to partially dehydrate the mixture.

DETAILED DESCRIPTION OF THE INVENTION

This invention is directed, in part, to novel lubricant compositions comprising a base oil of lubricating viscosity, dispersed hydrated alkali metal borate and a dispersant mixture comprising:

a) a polyalkylene succinic dispersant which is selected from the group consisting of a polyalkylene succinic anhydride, a non-nitrogen containing derivative of the polyalkylene succinic anhydride, mixtures of polyalkylene succinic anhydrides, mixtures of non-nitrogen containing derivatives of the polyalkylene succinic anhydride, and mixtures of one or more polyalkylene succinic anhydrides and one or more non-nitrogen containing derivatives of the polyalkylene succinic anhydride; and

b) a metal salt of a polyisobutenyl sulfonate.

Each of these components in the claimed composition will be defined herein.

The Dispersed Hydrated Alkali Metal Borate

Hydrated alkali metal borates are well known in the art. Representative patents disclosing suitable borates and methods of manufacture include: U.S. Pat. Nos. 3,313,727; 3,819,521; 3,853,772; 3,912,643; 3,997,454; and 4,089, 790.[1-6]

The hydrated alkali metal borates can be represented by the following formula:

$$M_2O.mB_2O_3.nH_2O$$

where M is sodium or potassium, m is a number preferably from 2.5 to 4.5 (both whole and fractional), and n is a number preferably from 1.0 to 4.8. Preferred hydrated alkali metal borates are hydrated potassium borates and more preferably the hydrated sodium borates because of their improved water tolerance. Most preferred are the hydrated sodium borates having a sodium-to-boron ratio of about 1:3. In another of its preferred embodiment, the hydrated borate particles generally have a mean particle size of less than 1 micron.

The hydrated alkali metal borates will generally comprise about 10 to 75 weight percent, preferably 25 to 50 weight percent, more preferably about 35 to 40 weight percent of the lubricant composition. (Unless otherwise stated, all percentages are in weight percent based on the total weight of the composition.)

The hydrated alkali metal borate dispersions have been found to be reactive in the presence of water. The presence of water has been found to alter the size, shape, and composition of the dispersed, amorphous borate particles to ultimately produce a number of crystalline borates which generally separate out from the oil phase to form deposits in the oil, and can damage the elastomer seals in various engine parts and cause leakage.

We have also found that sodium borates give better water tolerance and compatibility than potassium borates.

Preferably, the hydrated alkali metal borates contain small amounts of a water soluble oxo anion. Only from 0.001 moles to 0.11 moles of water soluble oxo anion should be present per mole of boron. This water-soluble oxo anion can include nitrate, sulfate, carbonate, phosphate, pyrophosphate, silicate, aluminate, germanate, stannate, zincate, plumbate, titanate, molybdate, tungstate, vanadate, niobate, tantalate, uranates, or can include the isopolymolybdates and isopolytungstates, or the heteropolymolybdates and heteropolytungstates, or mixtures thereof.

The presence of small amounts of water soluble oxo anions in the alkali metal borates is thought to improve the water tolerance of the alkali metal borates by disrupting the crystal structure of the hydrolysis products. This results in a lower tendency to form crystals or in a reduced rate of crystallization.

Preferred hydrated alkali metal borates include hydrated sodium borates particularly those characterized by a hydroxyl:boron ratio (OH:B) of from about 0.8:1 to 1.6: 1, preferably about 0.9:1 to 1.50: 1, and by a sodium to boron ratio of from about 1:2.75 to 1:3.25. Even more preferred hydrated sodium metal borates are those having a hydroxyl:boron ratio of from about 1.00:1 to 1.40:1 and a sodium to boron ratio of about 1:3.

In this regard, the term "hydroxyl:boron ratio" or "OH:B" refers to the number of hydroxyl groups attached to boron (moles of hydroxyl groups per mole of boron) in the dispersed hydrated alkali metal borate compositions as exemplified, for example, by the structure below. For the purposes of this application, the OH:B ratio of a hydrated sodium borate is calculated from the maximum infra-red, IR, absorbance between 3800 and 3250 cm^{-1} corrected by subtracting the baseline which is taken to be the absorbance at 3900 cm^{-1} of a 5.000% solution of the dispersed hydrated alkali metal borate in an oil of lubricating viscosity wherein all interfering absorbances due to other compounds or impurities have been subtracted. The remaining absorbance in this range corresponds to the hydroxyl groups of the dispersed sodium borate which is then converted to the OH:B ratio as follows:

$$OH:B=21.0A_{max}/\%B$$

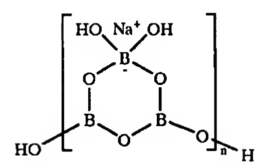
where A_{max} is the IR absorbance (peak height in the region of 3800 to 3250 cm^{-1}); and

%B is the percent boron in the original (non-diluted) dispersed sodium borate sample.

The absorbance in this range, 3800 to 3250 cm^{-1} corresponds to the hydroxyl groups of the sodium borate oligomer complex. If other additives are added to mask or interfere with the absorbance within this preferred range such groups will be subtracted from the IR spectra in the initial calculation of the OH:B measurement.

This absorbance is measured with a Nicolet 5DXB FTIR Spectrometer fitted with a DTGS detector and CsI beam splitter. The spectrometer has CaF_2 windows with 0.2 mm Teflon® spacer with small section cut out and a suitable cell holder. A spectrum of the sample is obtained using a 4 cm^{-1} resolution.

These sodium metal borates, having a 1:3 ratio of sodium to boron, can generally be represented by the following theoretical formula:



where n is a number preferably from 1.0 to 10.

Dispersed alkali metal borate compositions are generally prepared by forming, in deionized water, a solution of alkali metal hydroxide and boric acid optionally in the presence of a small amount of alkali metal carbonate. The solution is then added to a lubricant composition comprising an oil of lubricating viscosity, a dispersant mixture of the polyalkylene succinic dispersant and polyisobutenyl sulfonate as described above and any optional additives to be included therein (e.g., a detergent, 2,2'-thiodiethanol, and the like) to form an emulsion that is then dehydrated. Dehydration proceeds in three steps including an initial step of water removal that is initiated at a temperature of slightly over 100° C. This initial step is followed by a slow increase in temperature whereupon the emulsion changes from turbid to clear. In the final step, there is a rapid increase in temperature and the liquid once again becomes turbid.

Formation of the hydrated alkali metal borates described herein is achieved by stoichiometric selection of the appropriate amounts of alkali metal hydroxide and boron trioxide and control of the extent of dehydration such that the resulting product has the desired ratio of alkali metal to boron and the desired ratio of hydroxyl to boron.

The dehydration of the reaction mixture is carefully controlled (i.e. using a slower dehydration rate or employing a sweep gas, and the like) in order to avoid condensation of water on the walls of the reaction chamber. Condensation can result in water droplets in the lubricant composition which, in turn, can lead to undesired precipitate formation as described above. Such precipitate formation typically results in large particles that fall from suspension and have deleterious properties as previously noted. Accordingly, in a preferred embodiment of this invention, dehydration occurs over a period of from about 3 to 8 hours.

In a particularly preferred embodiment, the hydrated alkali metal borate particles generally have a mean particle size of less than 1 micron.

The Polyalkylene Succinic Dispersant

The polyalkylene succinic dispersant can be a polyalkylene succinic anhydride or a non-nitrogen containing derivative of the polyalkylene succinic anhydride and is preferably selected from the group consisting of a polyalkylene succinic anhydride, a non-nitrogen containing derivative of the polyalkylene succinic anhydride, mixtures of polyalkylene succinic anhydrides, mixtures of non-nitrogen containing derivatives of the polyalkylene succinic anhydride, and mixtures of one or more polyalkylene succinic anhydrides and one or more non-nitrogen containing derivatives of the polyalkylene succinic anhydride. Non-nitrogen containing derivatives of polyalkylene succinic anhydrides preferably include, succinic acids, Group I and/or Group II mono- or di-metal salts of succinic acids, succinate esters formed by the reaction of a polyalkylene succinic anhydride, acid chloride, or other derivatives with an alcohol (e.g., HOR' where R' is alkyl of from 1 to 10) and the like.

The polyalkylene succinic anhydride is preferably a polyisobutenyl succinic anhydride. In one preferred embodiment, the polyalkylene succinic anhydride is a polyisobutenyl succinic anhydride having a number average molecular weight of at least 500, more preferably at least 900–3000 and still more preferably from at least about 900 to about 2300.

In another preferred embodiment, a mixture of polyalkylene succinic anhydrides is employed. In this embodiment, the mixture preferably comprises a low molecular weight polyalkylene succinic anhydride component and a high molecular weight polyalkylene succinic anhydride component. More preferably, the low molecular weight component has a number average molecular weight of from about 500 to below 1000 and the high molecular weight component has a number average molecular weight of from 1000 to about 3000. Still more preferably, both the low and high molecular weight components are polyisobutenyl succinic anhydrides.

Preferably, the dispersed hydrated alkali metal borate is employed in a weight ratio of at least 2:1 relative to the polyalkylene succinic anhydride dispersant while being in the range of 2:1 to 10:1. In a preferred embodiment· the weight ratio is at least 4:1. In a preferred embodiment, mixtures as defined above of the polyalkylene succinic anhydrides are employed.

The polyalkylene succinic anhydride is the reaction product of a polyalkylene (preferably polyisobutene) with maleic anhydride. One can use conventional polyisobutene, or high methylvinylidene polyisobutene in the preparation of such polyalkylene succinic anhydrides. One can use thermal, chlorination, free radical, acid catalyzed, or any other process in this preparation. Examples of suitable polyalkylene succinic anhydrides are thermal PIBSA (polyisobutenyl succinic anhydride) described in U.S. Pat. No. 3,361,673; chlorination PIBSA described in U.S. Pat. No. 3,172,892; a mixture of thermal and chlorination PIBSA described in U.S. Pat. No. 3,912,764; high succinic ratio PIBSA described in U.S. Pat. No. 4,234,435; PolyPIBSA described in U.S. Pat. Nos. 5,112,507 and 5,175,225; high succinic ratio PolyPIBSA described in U.S. Pat. Nos. 5,565,528 and 5,616,668; free radical PIBSA described in U.S. Pat. Nos. 5,286,799, 5,319,030, and 5,625,004; PIBSA made from high methylvinylidene polybutene described in U.S. Pat. Nos. 4,152,499, 5,137,978, and 5,137,980; high succinic ratio PIBSA made from high methylvinylidene polybutene described in European Patent Application Publication No. EP 355 895; terpolymer PIBSA described in U.S. Pat. No. 5,792,729; sulfonic acid PIBSA described in U.S. Pat. No. 5,777,025 and European Patent Application Publication No. EP 542 380; and purified PIBSA described in U.S. Pat. No. 5,523,417 and European Patent Application Publication No. EP 602 863. The disclosures of each of these documents is incorporated herein by reference in their entirety.

The number average molecular weight of the polyalkylene tail in the polyalkylene succinic anhydride should be from about 300 to about 5000. This should be compatible with the previous ranges given before with the particular molecular weight depending on dispersant or mixture of dispersants to be employed. Preferably, the polyalkylene succinic anhydride component comprises from 2 to 40 weight percent, more preferably 10 to 15 weight percent of the weight of the lubricant composition.

Most preferable is the case where the polyalkylene succinic anhydride component is a polyisobutenyl succinic anhydride.

This invention is based, in part, on the discovery that the combination of a polyalkylene succinic dispersant and a metal salt of a polyisobutenyl sulfonate provides enhanced water tolerance and lubricating oil compatibility, when used in lubricating compositions comprising an alkali metal borate. It has also been found that a mixture of polyalkylene succinic anhydrides can be effectively employed. The mixture preferably comprises a low molecular weight polyalkylene succinic anhydride component and a high molecular weight polyalkylene succinic anhydride component. Alternatively, various molecular weight polyalkylene succinic anhydride components can be combined as a dispersant.

The Polyisobutenyl Sulfonate Dispersant

The metal salts of polyisobutenyl sulfonates used in the compositions of this invention can be highly overbased metal sulfonates or low overbased metal sulfonates. In addition, the sulfonic acids themselves can also be used. Overbased metal sulfonates are well known in the art. Highly overbased metal sulfonates typically have a total base number (TBN) of from about 250 to about 500, whereas low overbased metal sulfonates typically have a TBN of from about 0 to about 150. Both highly overbased metal sulfonates and low overbased metal sulfonates are well known in the art.

The term "metal sulfonate" is intended to encompass the salts of sulfonic acids derived from polyisobutene. Such polyalkenyl sulfonic acids are the subject of U.S. Pat. No. 6,410,491, which is incorporated herein by reference in its entirety. They can be obtained by treating polyisobutene with sulfur trioxide or a similar sulfonating agent such as acetyl sulfate and the like. The acids thus obtained are known as polyisobutene sulfonic acids and the salts as metal

sulfonates. Suitable metals include the alkali metals (e.g., potassium, sodium, cesium), alkaline earth metals (e.g., magnesium, calcium, barium), of which calcium and barium are preferred.

The polyisobutene employed is of sufficient molecular weight to provide oil-solubility to the polyisobutenyl sulfonic acid or metal salt thereof. Suitably, polyisobutenes having a number average molecular weight of from at least about 200 are employed. Preferably, the polyisobutene has a numbered average molecular weight of from about 200 to about 3000; more preferably, from about 300 to 2000; still more preferably, from about 400 to 1200; and even more preferably from about 500 to 1100.

Suitable polyisobutenes are commercially available or can be prepared by art recognized techniques such as those disclosed in U.S. Pat. No. 4,605,808 to Samson, issued Aug. 12, 1986, which is incorporated by reference in its entirety.

Preferably, the polyisobutenyl sulfonates are derived from high methyl-vinylidene isomers and/or 1,1-dialkyl isomer, preferably a 1,1-dimethyl isomer. More preferably the polyisobutene sulfonates are high methylvinylidene polyisobutenyl sulfonates or a mixture of such.

Preferably, the polyisobutenyl sulfonate is a low overbased calcium polyisobutenyl sulfonate having a TBN of from about 14–17 and comprises from 0.5 to 20 weight percent, more preferably 2 to 10 weight percent of the lubricant composition.

In one preferred embodiment, the ratio of polyisobutenyl sulfonate dispersant to the hydrated alkali metal borate employed in the composition is from about 0.05:1 to 1:1 and more preferably about 0.11:1.

In another preferred embodiment, the ratio of the polyalkylene succinic dispersant to the polyisobutenyl sulfonate used in the dispersant mixture is from about 4:1 and more preferably from about 2.6:1.

The Oil of Lubricating Viscosity

The lubricating oil to which the borates and the dispersant mixture are added can be any hydrocarbon-based lubricating oil or a synthetic base oil stock. The hydrocarbon-based lubricating oils may be derived from synthetic or natural sources and may be paraffinic, naphthetic or asphaltenic base, or mixtures thereof. The diluent oil can be natural or synthetic, and can be different viscosity grades.

The lubricating oil comprises from 30 to 70 weight percent, more preferably from 45 to 55 weight percent of the lubricant composition.

Formulations

The dispersed hydrated alkali metal borate compositions of the present invention (as described herein above) are generally blended to form additive packages comprising such dispersed hydrated alkali metal borate compositions. These additive packages typically comprise from about 10 to 75 weight percent of the dispersed hydrated alkali metal borate composition described above and from about 90 to 15 weight percent of one or more of conventional additives selected from the group consisting of ashless dispersants (0–5%), detergents (0–2%), sulfurized hydrocarbons (0–30%), dialkyl hydrogen phosphates (0–10%), zinc dithiophosphates (0–20%), dialkyl hydrogen phosphates (0–10%), pentaerythritol monooleate (0–10%), 2,5-dimercaptothiadiazole (0–5%), benzotriazole (0–5%), dispersed molybdenum disulfide (0–5%), imidazolines (0–10%), and foam inhibitors (0–2%) and the like wherein each weight percent is based on the total weight of the composition.

Fully formulated finished oil compositions of this invention can be formulated from these additive packages upon further blending with an oil of lubricating viscosity. Preferably, the additive package described above is added to an oil of lubricating viscosity in an amount of from about 5 to 15 weight percent to provide for the finished oil composition wherein the weight percent of the additive package is based on the total weight of the composition. More preferably, added along with the oil of lubricating viscosity is a polymethacrylate viscosity index improver which is included at a level of 0–12% and/or a pour point depressant at a level of 0–1%, to form a finished oil wherein the weight percent of each of the viscosity index improver and pour point depressant is based on the total weight of the composition.

A variety of other additives can be present in lubricating oils of the present invention. Those additives include antioxidants, rust inhibitors, corrosion inhibitors, extreme pressure agents, antifoam agents, other viscosity index improvers, other anti-wear agents, and a variety of other well-known additives in the art.

EXAMPLES

The invention will be further illustrated by the following examples, which set forth particularly advantageous method embodiments. While the examples are provided to illustrate the present invention, they are not intended to limit it.

As used herein, the following abbreviations have the following meanings. If not defined, the abbreviation will have its art recognized meaning.

cSt =	centistokes
g =	gram
IR =	infra-red
LOB =	low overbased
M =	metal
mm =	millimeters
mL =	milliliter
Mn or M_n 32	number average molecular weight
NTU or ntu =	nephelometric turbidity unit
PIB =	polyisobutylene
PIBS =	polyisobutenyl sulfonate
PIBSA =	polyisobutenyl succinic anhydride
PSD =	particle size distribution (microns)
TBN =	total base number (mgKOH/g)
vis =	viscosity

Example 1

A dispersed alkali metal borate composition is prepared by dehydrating a water-in-oil emulsion of an aqueous solution of an alkali metal hydroxide and boric acid. Preferably a solution is prepared having an alkali metal to boron ratio of 1 to 3.

This solution is then added to a combination of neutral oil, succinic dispersant, and a polyisobutenyl (PIB) sulfonate and mixed to form an emulsion. The resulting emulsion is heated to partially dehydrate it. Reduced pressures can also be used and the temperature set accordingly. During dehydration of the emulsion there is an initial period when water is removed from the emulsion at a rapid rate at a constant temperature for example at about 102° C. After this period, nearly all process water has been eliminated and water removed after this stage is due to the dehydration of the hydrated borate oligomer. Then the temperature slowly increases and the emulsion changes from turbid to clear. As the degree of dehydration and temperature continue to increase, the resulting liquid will again become turbid.

Sodium Borate Dispersions:

A hydrated sodium borate dispersion was prepared by dehydration of an oil-in-water emulsion of an aqueous sodium borate and a succinic dispersant/PIB sulfonate oil solution by heating it to 270° F. for about 3 hours. The aqueous solution was prepared in 2 liter glass beaker by stirring and heating mixtures of: 136.4 g of deionized water, 109.8 g of 99.5% Boric Acid (EMScience), 46.8 g of 50% Sodium Hydroxide in water (VWR), and 0.30 g of 99.5% Sodium Carbonate (EMScience), until the boric acid completely dissolved. Oil-in-water emulsions were made by gradually adding the aqueous phase to an oil phase containing: 136.15 g of Exxon 150 Neutral oil, a group I base oil, 30.25 g of a polyisobutenyl alkenyl succinic anhydride having a molecular weight of about 1100 amu, and 13.25 g of a low overbased calcium polyisobutenyl sulfonate having a TBN of about 14–17 mgKOH/g and wherein the polyisobutenyl moiety has an average molecular weight of about 550 amu, under a vigorous mixing action. A high shear mixer is preferred to form an emulsion or a micro-emulsion.

The emulsion was then dehydrated in a 1-liter stainless steel kettle equipped with a mechanical stirrer, heat mantle, temperature controller, and nitrogen sweep line at a temperature of about 270° F. for a period of about 3 hours to provide a hydrated sodium borate composition having a hydroxyl:boron ratio of about 0.8:1 and a sodium to boron ratio of 3:1.

This composition contains approximately:

45 weight percent of the hydrated sodium borate;

13 weight percent of polyisobutenyl succinic anhydride;

5 weight percent of the calcium polyisobutenyl sulfonate; and the balance being the oil of lubricating viscosity.

Examples 2–4

In addition, using the procedure as described above, three other hydrated sodium borate compositions were prepared. Example 2 used a low overbased calcium polyisobutenyl sulfonate having a TBN of about 14–17 mgKOH/g and wherein the polyisobutenyl moiety has a number average molecular weight of about 1000 amu. Example 3 employed a calcium alkylaromatic sulfonate having a number average molecular weight of about 500 and a TBN of about 28 in place of the calcium polyisobutenyl sulfonate; and Example 4 employed a calcium natural sulfonate with a TBN of about 5, in place of the calcium polyisobutenyl sulfonate. All dispersants in the above examples were employed as a mixture with the same polyisobutenyl succinic anhydride at approximately the same ratio of 2.6:1. The other components in the hydrated sodium borate compositions were employed in approximately the same ratio as Example 1. These results are summarized in Table 1.

TABLE 1

Chemical and Physical Properties of Borate Dispersions

Ex	Dispersant Mixture PIBSA/Sulfonate	TBN	Turbidity Ntu	OH:B	PSD 90%	PSD 50%
1	PIBSA/Calcium polyisobutenyl sulfonate PIBS 550	121.5	17.4	0.81:1	0.18	0.14
2	PIBSA/Calcium polyisobutenyl sulfonate PIBS 1000	122.9	104	0.87:1	0.19	0.14
3	PIBSA/Calcium alkyl-aromatic sulfonate	123.3	84	0.72:1	0.19	0.15
4	PIBSA/Natural sulfonate	123.2	104	0.79:1	0.2	0.15

In Table 1, the column "PSD 90%" refers to particle size distribution and is a measure of particle size wherein at least 90% of the particles are less than the indicated value, in microns. Similarly, the column "PSD 50%" measures particle size wherein at least 50% of the particles are less than the indicated value, in microns.

Water Tolerance Performance

The water tolerance of a gear oil composition as a function of the dispersant mixture used was evaluated. Hydrated sodium borate compositions prepared similarly to that of Example 1 above were combined with additives to form fully formulated gear oil compositions. These were prepared by taking the borate lubricating compositions of Example 1, and blending at a dosage of about 46% into a typical additive package comprising, ashless dispersant, calcium sulfonate, corrosion inhibitor, EP agent, friction modifier, multifunctional additives, metal deactivator, etc. This additive package was then added at the level of 6.5% to diluent oil to make an 80W90 finished oil formulation. This formulation was then run in the Coordinating Research Counsel L-33 test, to test water tolerance; see U.S. Pat. No. 4,089,790 incorporated herein by reference.

Each of these gear oil formulations were then subjected to water contamination at elevated temperatures using the CRC L-33 test. This test evaluates lubricant performance by exposure of the lubricant to a severe environment. Performance is based upon deposit and rust conditions within the test equipment as well as the condition of the lubricant upon completion of the test. In this test, 1.2 liters of test lubricant are placed in a bench-mounted automotive differential assembly and water, approximately 30 milliliters, is added thus, simulating a type of severe filed service in which corrosion promoting moisture in the form of condensed water vapor has accumulated in the axle assembly. This test has been determined to correlate to field service. The results of this test are found in Table 2 below:

TABLE 2

Water Tolerance Data

Ex	Dispersant Mixture	L33 Deposits, Area %
1	Polyisobutenyl succinic anhydride/ calcium polyisobutenyl sulfonate PIBS 550	1
2	Polyisobutenyl succinic anhydride/ calcium polyisobutenyl sulfonate PIBS 1000	4.5
3	Polyisobutenyl succinic anhydride/ calcium alkyl-aromatic sulfonate	6
4	Polyisobutenyl succinic anhydride/ natural sulfonate	8.5

L33 deposits, area %, are the percentage of the differential housing and parts covered with deposits, as determined by the prescribed method. The results of this test illustrate that water tolerance for the compositions of this invention are significantly superior to those of conventional additive combinations.

From the foregoing description, various modifications and changes in the above described invention will occur to those skilled in the art. All such modifications coming within the scope of the appended claims are intended to be included therein.

What is claimed is:

1. A lubricant composition which comprises:

a base oil of lubricating viscosity;

a dispersed hydrated alkali metal borate; and

a dispersant mixture comprising:

a) a polyalkylene succinic dispersant which is selected from the group consisting of a polyalkylene succinic anhydride, a non-nitrogen containing derivative of the polyalkylene succinic anhydride, mixtures of polyalkylene succinic anhydrides, mixtures of non-nitrogen containing derivatives of the polyalkylene succinic anhydride, and mixtures of one or more polyalkylene succinic anhydrides and one or more non-nitrogen containing derivatives of the polyalkylene succinic anhydride; and

b) a metal salt of a polyisobutenyl sulfonate, wherein the polyisobutenyl moiety has a number average molecular weight from about 400 to 1200.

2. The lubricant composition according to claim 1, wherein the dispersed hydrated alkali metal borate is a dispersed hydrated sodium borate.

3. The lubricant composition according to claim 2, wherein the dispersed hydrated alkali metal borate is a dispersed hydrated sodium borate and has a sodium to boron ratio of from about 1:2.75 to about 1:3.25.

4. The lubricant composition according to claim 1, wherein the polyalkylene succinic anhydride is a polyisobutenyl succinic anhydride having a number average molecular weight of at least 500.

5. The lubricant composition according to claim 4, wherein the polyisobutenyl succinic anhydride has a number average molecular weight of from about 900 to about 3000.

6. The lubricant composition according to claim 1, comprising a mixture of polyalkylene succinic anhydrides, said mixture having a low number average molecular weight component of from 500 to below 1000, and having a high number average molecular weight component of from 1000 to about 3000.

7. The lubricant composition according to claim 1, wherein the dispersed hydrated alkali metal borate has a ratio of at least 2:1 relative to the dispersant mixture of polyalkylene succinic dispersant and polyisobutenyl sulfonate.

8. The lubricant composition according to claim 7, wherein the dispersed hydrated alkali metal borate has a ratio of from 2:1 to 10:1 relative to the dispersant mixture.

9. The lubricant composition according to claim 8, wherein the dispersed hydrated alkali metal borate has a ratio of about 5:2 relative to the dispersant mixture.

10. The lubricant composition according to claim 1, wherein the metal salt of a polyisobutenyl sulfonate is an alkali metal or alkaline earth metal salt.

11. The lubricant composition according to claim 10, wherein the metal salt of a polyisobutenyl sulfonate is an alkaline earth metal salt.

12. The lubricant composition according to claim 11, wherein the alkaline earth metal salt is calcium.

13. The lubricant composition according to claim 1, wherein the metal salt of a polyisobutenyl sulfonate has a polyisobutenyl moiety having a number average molecular weight of from about 500 to about 1100.

14. The lubricant composition according to claim 1, which further comprises from about 0.001 moles to about 0.11 moles of a water soluble oxo anion per mole of boron.

15. The lubricant composition according to claim 14, wherein said oxo anion is selected from the group consisting of nitrate, sulfate, carbonate, phosphate, pyrophosphate, silicate, aluminate, germanate, stannate, zincate, plumbate, titanate, molbydate, tungstate, vanadate, niobate, tantalate, uranate, isopolymolybdate, isopolytungstate, heteropolymolybdate, heteropolytungstates, and mixtures thereof.

16. A method for enhancing the water tolerance of lubricant compositions comprising alkali metal borate which method comprises adding an anti-wear effective amount of an alkali metal borate to a base oil of lubricating viscosity in combination with a dispersant effective amount of a dispersant mixture comprising:

a) a polyalkylene succinic dispersant which is selected from the group consisting of a polyalkylene succinic anhydride, a non-nitrogen containing derivative of the polyalkylene succinic anhydride, mixtures of polyalkylene succinic anhydrides, mixtures of non-nitrogen containing derivatives of the polyalkylene succinic anhydride, and mixtures of one or more polyalkylene succinic anhydrides and one or more non-nitrogen containing derivatives of the polyalkylene succinic anhydride; and

b) a metal salt of a polyisobutenyl sulfonate, wherein the polyisobutenyl moiety has a number average molecular weight from about 400 to 1200.

17. A method for preparing a lubricant composition comprising a base oil of lubricating viscosity, a dispersed hydrated alkali metal borate, and a dispersant mixture comprising:

a) a polyalkylene succinic dispersant which is selected from the group consisting of a polyalkylene succinic anhydride, a non-nitrogen containing derivative of the polyalkylene succinic anhydride, mixtures of polyalkylene succinic anhydrides, mixtures of non-nitrogen containing derivatives of the polyalkylene succinic anhydride and mixtures of one or more polyalkylene succinic anhydrides and one or more non-nitrogen containing derivatives of the polyalkylene succinic anhydride; and

b) a metal salt of a polyisobutenyl sulfonate, wherein the polyisobutenyl moiety has a number average molecular weight from about 400 to 1200;

which method comprises:

mixing, under agitation, (1) an aqueous solution of boric acid and alkali metal hydroxide, and (2) a diluent oil containing the polyalkylene succinic dispersant and the polyisobutenyl sulfonate; and

heating the mixture to remove the water.

18. The method according to claim 17 wherein the dispersed hydrated alkali metal borate is a dispersed hydrated sodium borate.

19. The lubricant composition according to claim 1, wherein the dispersed hydrated alkali metal borate is a dispersed hydrated sodium borate having a hydroxyl to boron ratio of from about 0.8:1 to 1.6:1.

* * * * *

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(54) LUBRICANT COMPOSITION COMPRISING ALKALI METAL BORATE AND POLYALKYLENE SUCCINIC ANHYDRIDE

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(57) ABSTRACT

Disclosed are lubricant compositions comprising a dispersed hydrated alkali metal borate and a polyalkylene succinic anhydride, a mixture of polyalkylene succinic anhydrides or derivatives thereof. Also disclosed are methods for improving the water tolerance of a lubricant composition comprising an alkali metal borate. Such methods employ compositions comprising a dispersed hydrated alkali metal borate and a polyalkylene succinic anhydride, a mixture of polyalkylene succinic anhydrides or derivatives thereof.

LUBRICANT COMPOSITION COMPRISING ALKALI METAL BORATE AND POLYALKYLENE SUCCINIC ANHYDRIDE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation-in-part of U.S. patent application Ser. No. 09/292,627, filed Apr. 15, 1999, which application is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] This invention is directed, in part, to novel lubricant compositions. These compositions comprise an alkali metal borate and a polyalkylene succinic anhydride, a mixture of polyalkylene succinic anhydrides or derivatives thereof. Surprisingly, these compositions have improved compatibility, extreme pressure properties and/or water tolerance over similar compositions comprising a dispersant other than a polyalkylene succinic anhydride or derivatives thereof.

[0003] This invention is also directed, in part, to methods for improving the water tolerance of a lubricant composition comprising an alkali metal borate. Such methods employ compositions comprising an alkali metal borate and a polyalkylene succinic anhydride, a mixture of polyalkylene succinic anhydrides or derivatives thereof.

[0004] References

[0005] The following references are cited in this application as superscript numbers:

[0006] [1] Peeler, U.S. Pat. No. 3,313,727, *Alkali Metal Borate E. P. Lubricants,* issued Apr. 11, 1967

[0007] [2] Adams, U.S. Pat. No.3,912,643, *Lubricant Containing Neutralized Alkali Metal Borates,* issued Oct. 14, 1975

[0008] [3] Sims, U.S. Pat. No. 3,819,521, *Lubricant Containing Dispersed Borate and a Polyol,* issued Jun. 25, 1974

[0009] [4] Adams, U.S. Pat. No. 3,853,772, *Lubricant Containing Alkali Metal Borate Dispersed with a Mixture of Dispersants,* issued Dec. 10, 1974

[0010] [5] Adams, U.S. Pat. No. 3,997,454, *Lubricant Containing Potassium Borate,* issued Dec. 14, 1976

[0011] [6] Adams, U.S. Pat. No. 4,089,790, *Synergistic Combinations of Hydrated Potassium Borate, Antiwear Agents, and Organic Sulfide Antioxidants,* issued May 16, 1978

[0012] [7] Adams, U.S. Pat. No. 4,163,729, *Synergistic Combinations of Hydrated Potassium Borate, Antiwear Agents, and Organic Sulfide Antioxidants,* issued Aug. 7, 1979

[0013] [8] Frost, U.S. Pat. No. 4,263,155, *Lubricant Composition Containing an Alkali Metal Borate and a Sulfur-Containing Polyhydroxy Compound,* U.S. Pat. No. 5,461,184, issued Oct. 24, 1995

[0014] [9] Frost, U.S. Pat. No.4,401,580, *Lubricant Composition Containing an Alkali Metal Borate and an Ester-Polyol Compound,* issued Aug. 30, 1983

[0015] [10] Frost, U.S. Pat. No. 4,472,288, *Lubricant Composition Containing an Alkali Metal Borate and an Oil-Soluble Amine Salt of a Phosphorus Compound,* issued Sep. 18, 1984

[0016] [11] Clark, U.S. Pat. No.4,584,873, *Automotive Friction Reducing Composition,* issued Aug. 13, 1985

[0017] [12] Brewster, U.S. Pat. No. 3,489,619, *Heat Transfer and Quench Oil,* issued Jan. 13, 1970

[0018] All of the above references are herein incorporated by reference in their entirety to the same extent as if each individual publication or patent was specifically and individually indicated to be incorporated by reference in its entirety.

[0019] State of the Art

[0020] High load conditions often occur in gear sets such as those used in automobile transmissions and differentials, pneumatic tools, gas compressors, centrifuges, high-pressure hydraulic systems, metal workings and similar devices as well as in many types of bearings. When employed in such environments, it is conventional to add an extreme-pressure agent to the lubricant composition and, in this regard, alkali metal borates are well known extreme-pressure agents for such compositions.[1-12]

[1] Peeler, U.S. Pat. No. 3,313,727, *Alkali Metal Borate E. P. Lubricants,* issued Apr. 11, 1967

[2] Adams, U.S. Pat. No.3,912,643, *Lubricant Containing Neutralized Alkali Metal Borates,* issued Oct. 14, 1975

[3] Sims, U.S. Pat. No. 3,819,521, *Lubricant Containing Dispersed Borate and a Polyol,* issued Jun. 25, 1974

[4] Adams, U.S. Pat. No. 3,853,772, *Lubricant Containing Alkali Metal Borate Dispersed with a Mixture of Dispersants,* issued Dec. 10, 1974

[5] Adams, U.S. Pat. No. 3,997,454, *Lubricant Containing Potassium Borate,* issued Dec. 14, 1976

[6] Adams, U.S. Pat. No. 4,089,790, *Synergistic Combinations of Hydrated Potassium Borate, Antiwear Agents, and Organic Sulfide Antioxidants,* issued May 16, 1978

[7] Adams, U.S. Pat. No. 4,163,729, *Synergistic Combinations of Hydrated Potassium Borate, Antiwear Agents, and Organic Sulfide Antioxidants,* issued Aug. 7, 1979

[8] Frost, U.S. Pat. No. 4,263,155, *Lubricant Composition Containing an Alkali Metal Borate and a Sulfur-Containing Polyhydroxy Compound,* U.S. Pat. No. 5,461,184, issued Oct. 24, 1995

[9] Frost, U.S. Pat. No.4,401,580, *Lubricant Composition Containing an Alkali Metal Borate and an Ester-Polyol Compound,* issued Aug. 30, 1983

[10] Frost, U.S. Pat. No. 4,472,288, *Lubricant Composition Containing an Alkali Metal Borate and an Oil-Soluble Amine Salt of a Phosphorus Compound,* issued Sep. 18, 1984

[11] Clark, U.S. Pat. No.4,584,873, *Automotive Friction Reducing Composition,* issued Aug. 13, 1985

[12] Brewster, U.S. Pat. No. 3,489,619, *Heat Transfer and Quench Oil,* issued Jan. 13, 1970

[0021] Because the alkali metal borate is insoluble in lubricant oil media, it is conventional to include a dispersant in such compositions in order to facilitate the formation of a homogenous dispersion. Examples of dispersants include lipophilic surface-active agents such as alkenyl succinimides or other nitrogen containing dispersants.[1-4] It is also conventional to employ the alkali metal borate at particle sizes of less than 1 micron in order to facilitate the formation of the homogenous dispersion.[11]

[1] Peeler, U.S. Pat. No. 3,313,727, *Alkali Metal Borate E. P. Lubricants,* issued Apr. 11, 1967

[2] Adams, U.S. Pat. No.3,912,643, *Lubricant Containing Neutralized Alkali Metal Borates*, issued Oct. 14, 1975

[3] Sims, U.S. Pat. No. 3,819,521, *Lubricant Containing Dispersed Borate and a Polyol*, issued Jun. 25, 1974

[4] Adams, U.S. Pat. No. 3,853,772, *Lubricant Containing Alkali Metal Borate Dispersed with a Mixture of Dispersants*, issued Dec. 10, 1974

[11] Clark, U.S. Pat. No.4,584,873, *Automotive Friction Reducing Composition*, issued Aug. 13, 1985

[0022] The use of alkali metal borates in lubricant compositions is complicated by the presence of water in the environment where the composition is employed. Conventional preparation methods remove essentially all the water from the media[12]. However, when the presence of water exceeds a threshold concentration in the lubricant composition, the borate crystallizes out of the composition and forms hard granules. These granules cause severe noise in the lubricated systems and can severely damage the gears or bearings themselves as well as leading to seal leakage.[10] Further, borate lost by crystallization decreases the extreme pressure properties of the lubricant composition.

[10] Frost, U.S. Pat. No. 4,472,288, *Lubricant Composition Containing an Alkali Metal Borate and an Oil-Soluble Amine Salt of a Phosphorus Compound*, issued Sep. 18, 1984

[12] Brewster, U.S. Pat. No. 3,489,619, *Heat Transfer and Quench Oil*, issued Jan. 13, 1970

[0023] On the other hand, lubricant compositions employing alkali metal borates are often employed in environments where water is invariably present.

[0024] In view of the above, enhanced water tolerance of lubricant compositions comprising an alkali metal borate would be particularly beneficial.

SUMMARY OF THE INVENTION

[0025] This invention is directed to the novel and unexpected discovery that enhanced water tolerance and lubricant oil compatibility for alkali metal borates can be achieved by employing a dispersant selected from the group consisting of a polyalkylene succinic anhydride, a non-nitrogen containing derivative of the polyalkylene succinic anhydride and mixtures of polyalkylene succinic anhydrides, mixtures of non-nitrogen containing derivatives of the polyalkylene succinic anhydride or mixtures of both polyalkylene succinic anhydrides and non-nitrogen containing derivatives of the polyalkylene succinic anhydride.

[0026] Accordingly, in one of its composition aspects, this invention is directed to a lubricant composition which comprises a base oil of lubricating viscosity, a dispersed hydrated alkali metal borate, and a dispersant that is selected from the group consisting of a polyalkylene succinic anhydride, a non-nitrogen containing derivative of the polyalkylene succinic anhydride, mixtures of polyalkylene succinic anhydrides, mixtures of non-nitrogen containing derivatives of the polyalkylene succinic anhydride and mixtures of both polyalkylene succinic anhydrides and non-nitrogen containing derivatives of the polyalkylene succinic anhydride.

[0027] In addition to improved water tolerance, it has now been discovered that the use of such dispersants in these lubricant compositions gives far superior compatibility than other possible dispersants.

[0028] Preferably, the dispersed hydrated alkali metal borate is a dispersed hydrated sodium borate. A preferred dispersed hydrated sodium borate has a sodium to boron metal ratio of from about 1:2.5 to about 1:4.5 and more preferably about 1:3.

[0029] Preferably, the hydrated alkali metal borate contains small amounts of a water soluble oxo anion. Only from 0.001 moles to 0.11 moles of water soluble oxo anion should be present per mole of boron. This water-soluble oxo anion can include nitrate, sulfate, carbonate, phosphate, pyrophosphate, silicate, aluminate, germanate, stannate, zincate, plumbate, titanate, molybdate, tungstate, vanadate, niobate, tantalate, uranates, or can include the isopolymolybdates and isopolytungstates, or the heteropolymolybdates and heteropolytungstates, or mixtures thereof.

[0030] Preferably, the dispersant is a polyalkylene succinic anhydride or a mixture of polyalkylene succinic anhydrides. More preferably, the polyalkylene succinic anhydride is a polyisobutenyl succinic anhydride. In one preferred embodiment, the polyalkylene succinic anhydride is a polyisobutenyl succinic anhydride having a number average molecular weight of at least 500, more preferably at least 900 and still more preferably from at least about 900 to about 3000.

[0031] Preferably, the dispersed hydrated alkali metal borate is present in a ratio of at least 2:1 relative to the polyalkylene succinic anhydride dispersant. More preferably the ratio of dispersed hydrated alkali metal borate to dispersant is from 2:1 up to 10:1. Most preferably the ratio is at least 5:2. In a preferred embodiment, the dispersed hydrated alkali metal borate is a hydrated sodium metal borate, preferably a NaB_3 condensed borate and the polyalkylene succinic anhydride is a polyisobutenyl succinic anhydride.

[0032] In another preferred embodiment, a mixture of polyalkylene succinic anhydrides are employed. In this embodiment, the mixture preferably comprises a low molecular weight polyalkylene succinic anhydride component and a high molecular weight polyalkylene succinic anhydride component. More preferably, the low molecular weight component has a number average molecular weight of from about 500 to below 1000 and the high molecular weight component has a number average molecular weight of from 1000 to about 3000. Still more preferably, both the low and high molecular weight components are polyisobutenyl succinic anhydrides.

[0033] Preferably, the lubricant composition also comprises a detergent, such as a metal sulfonate. A preferred metal sulfonate is a calcium alkyl aromatic sulfonate.

[0034] This invention is also directed to methods for enhancing the water tolerance of lubricant compositions comprising alkali metal borate. Accordingly, in one of its method aspects, this invention is directed to a method for enhancing the water tolerance of lubricant compositions comprising alkali metal borate which method comprises adding an anti-wear effective amount of a dispersed hydrated alkali metal borate to a base oil of lubricating viscosity in combination with a dispersant effective amount of a dispersant selected from the group consisting of a polyalkylene succinic anhydride, a non-nitrogen containing derivative of the polyalkylene succinic anhydride, mixtures of polyalkylene succinic anhydrides, mixtures of non-nitrogen containing derivatives of the polyalkylene succinic

anhydride and mixtures of both polyalkylene succinic anhydrides and non-nitrogen containing derivatives of the polyalkylene succinic anhydride.

[0035] This invention is still further directed to methods for the preparation of such lubricant compositions. Accordingly, in another of its method aspects, this invention is directed to a method for preparing a lubricant composition comprising a base oil of lubricating viscosity, a dispersed hydrated alkali metal borate, and a polyalkylene succinic dispersant that is selected from the group consisting of a polyalkylene succinic anhydride, a non-nitrogen containing derivative of the polyalkylene succinic anhydride, mixtures of polyalkylene succinic anhydrides, mixtures of non-nitrogen containing derivatives of the polyalkylene succinic anhydride and mixtures of both polyalkylene succinic anhydrides and non-nitrogen containing derivatives of the polyalkylene succinic anhydride which method comprises:

[0036] mixing, under agitation, (1) an aqueous solution of boric acid and alkali metal hydroxide, and (2) a diluent oil containing the polyalkylene succinic dispersant (and any metal sulfonate); and then heating the mixture to remove the water. Preferably the lubricant composition comprises a hydrated sodium borate and, more preferably, the hydrated sodium borate has a hydroxyl to boron ratio (OH:B) of from about 0.8:1 to 1.6:1, preferably from about 0.9:1 to 1.50:1, and more preferably from about 1.00:1 to 1.40: 1, as disclosed in concurrently filed U.S. application Ser. No. ___,___ (Attorney Docket No. 005950-699, T-5928) and entitled "Dispersed Hydrated Sodium Borate Compositions Having Improved Properties In Lubricating Oil Compositions" which is incorporated herein by reference in its entirety.

DETAILED DESCRIPTION OF THE INVENTION

[0037] This invention is directed, in part, to novel lubricant compositions comprising a base oil of lubricating viscosity, a dispersed hydrated alkali metal borate and a dispersant selected from the group consisting of a polyalkylene succinic anhydride, a non-nitrogen containing derivative of the polyalkylene succinic anhydride, mixtures of polyalkylene succinic anhydrides, mixtures of non-nitrogen containing derivatives of the polyalkylene succinic anhydride and mixtures of both polyalkylene succinic anhydrides and non-nitrogen containing derivatives of the polyalkylene succinic anhydride.

[0038] Each of these components in the claimed composition will be defined herein.

[0039] The Dispersed Hydrated Alkali Metal Borate

[0040] Hydrated alkali metal borates are well known in the art. Representative patents disclosing suitable borates and methods of manufacture include: U.S. Pat. Nos. 3,313,727; 3,819,521; 3,853,772; 3,912,643; 3,997,454; and 4,089,790.[1-6]

[1] Peeler, U.S. Pat. No. 3,313,727, *Alkali Metal Borate E. P. Lubricants*, issued Apr. 11, 1967

[2] Adams, U.S. Pat. No.3,912,643, *Lubricant Containing Neutralized Alkali Metal Borates*, issued Oct. 14, 1975

[3] Sims, U.S. Pat. No. 3,819,521, *Lubricant Containing Dispersed Borate and a Polyol*, issued Jun. 25, 1974

[4] Adams, U.S. Pat. No. 3,853,772, *Lubricant Containing Alkali Metal Borate Dispersed with a Mixture of Dispersants*, issued Dec. 10, 1974

[5] Adams, U.S. Pat. No. 3,997,454, *Lubricant Containing Potassium Borate*, issued Dec. 14, 1976

[6] Adams, U.S. Pat. No. 4,089,790, *Synergistic Combinations of Hydrated Potassium Borate, Antiwear Agents, and Organic Sulfide Antioxidants*, issued May 16, 1978

[0041] The hydrated alkali metal borates can be represented by the following formula:

$$M_2O \cdot mB_2O_3 \cdot nH_2O$$

[0042] where M is sodium or potassium, m is a number preferably from 2.5 to 4.5 (both whole and fractional), and n is a number preferably from 1.0 to 4.8. Preferred hydrated alkali metal borates are hydrated potassium borates and more preferably the hydrated sodium borates because of their improved water tolerance. Most preferred are the hydrated sodium borates having a sodium-to-boron ratio of about 1:3. In another of its preferred embodiment, the hydrated borate particles generally have a mean particle size of less than 1 micron.

[0043] The hydrated alkali metal borates will generally comprise about 10 to 75 weight percent, preferably 25 to 50 weight percent, more preferably about 35 to 40 weight percent of the lubricant composition. (Unless otherwise stated, all percentages are in weight percent.) The hydrated alkali metal borate dispersions have been found to be reactive in the presence of water. The presence of water has been found to alter the size, shape, and composition of the dispersed, amorphous borate particles, which have the overall composition $MB_3O_5H_2O$, to ultimately produce a number of crystalline borates which have the compositions $MB_3O_5 \cdot 3H_2O$, $MB_5O_8 \cdot 4H_2O$, $M_2B_5O_8(OH) \cdot 2H_2O$, $M_2B_4O_7 \cdot 4H_2O$, and the like. These crystals generally separate out from the oil phase to form deposits in the oil, and can damage the elastomer seals in various engine parts and cause leakage.

[0044] We have also found that sodium borates give better water tolerance and compatibility than potassium borates.

[0045] Preferably, the hydrated alkali metal borates contain small amounts of a water soluble oxo anion. Only from 0.001 moles to 0.11 moles of water soluble oxo anion should be present per mole of boron. This water-soluble oxo anion can include nitrate, sulfate, carbonate, phosphate, pyrophosphate, silicate, aluminate, germanate, stannate, zincate, plumbate, titanate, molybdate, tungstate, vanadate, niobate, tantalate, uranates, or can include the isopolymolybdates and isopolytungstates, or the heteropolymolybdates and heteropolytungstates, or mixtures thereof.

[0046] The presence of small amounts of water soluble oxo anions in the alkali metal borates is thought to improve the water tolerance of the alkali metal borates by disrupting the crystal structure of the hydrolysis products. This results in a lower tendency to form crystals or in a reduced rate of crystallization.

[0047] The Polyalkylene Sussinic Dispersant

[0048] The dispersant can be a polyalkylene succinic anhydride or a non-nitrogen containing derivative of the polyalkylene succinic anhydride and is preferably selected from the group consisting of a polyalkylene succinic anhydride, a non-nitrogen containing derivative of the polyalkylene succinic anhydride, mixtures of polyalkylene succinic

anhydrides, mixtures of non-nitrogen containing derivatives of the polyalkylene succinic anhydride and mixtures of both polyalkylene succinic anhydrides and non-nitrogen containing derivatives of the polyalkylene succinic anhydride. Non-nitrogen containing derivatives of polyalkylene succinic anhydrides preferably include, succinic acids, Group I and/or Group II mono- or di-metal salts of succinic acids, succinate esters formed by the reaction of a polyalkylene succinic anhydride, acid chloride, or other derivative with an alcohol and the like.

[0049] The polyalkylene succinic anhydride is preferably a polyisobutenyl succinic anhydride. In one preferred embodiment, the polyalkylene succinic anhydride is a polyisobutenyl succinic anhydride having a number average molecular weight of at least 500, more preferably at least 900-3000 and still more preferably from at least about 900 to about 2300.

[0050] In another preferred embodiment, a mixture of polyalkylene succinic anhydrides are employed. In this embodiment, the mixture preferably comprises a low molecular weight polyalkylene succinic anhydride component and a high molecular weight polyalkylene succinic anhydride component. More preferably, the low molecular weight component has a number average molecular weight of from about 500 to below 1000 and the high molecular weight component has a number average molecular weight of from 1000 to about 3000. Still more preferably, both the low and high molecular weight components are polyisobutenyl succinic anhydrides.

[0051] Preferably, the dispersed hydrated alkali metal borate is employed in a weight ratio of at least 2:1 relative to the polyalkylene succinic anhydride dispersant, while being more preferably in the range of 2:1 to 10:1. Most preferably, the ratio is at least 5:2. In a preferred embodiment, mixtures as defined above of the polyalkylene succinic anhydrides are employed.

[0052] The polyalkylene succinic anhydride is the reaction product of a polyalkylene (preferably polyisobutene) with maleic anhydride. One can use conventional polyisobutene, or high methylvinylidene polyisobutene in the preparation of such polyalkylene succinic anhydrides. One can use thermal, chlorination, free radical, acid catalyzed, or any other process in this preparation. Examples of suitable polyalkylene succinic anhydrides are thermal PIBSA (polyisobutenyl succinic anhydride) described in U.S. Pat. No. 3,361,673; chlorination PIBSA described in U.S. Pat. No. 3,172,892; a mixture of thermal and chlorination PIBSA described in U.S. Pat. No. 3,912,764; high succinic ratio PIBSA described in U.S. Pat. No. 4,234,435; PolyPIBSA described in U.S. Pat. Nos. 5,112,507 and 5,175,225; high succinic ratio PolyPIBSA described in U.S. Pat. Nos. 5,565,528 and 5,616,668; free radical PIBSA described in U.S. Pat. Nos. 5,286,799, 5,319,030, and 5,625,004; PIBSA made from high methylvinylidene polybutene described in U.S. Pat. Nos. 4,152,499, 5,137,978, and 5,137,980; high succinic ratio PIBSA made from high methylvinylidene polybutene described in European Patent Application Publication No. EP 355 895; terpolymer PIBSA described in U.S. Pat. No. 5,792,729; sulfonic acid PIBSA described in U.S. Pat. No. 5,777,025 and European Patent Application Publication No. EP 542 380; and purified PIBSA described in U.S. Pat. No. 5,523,417 and European Patent Application Publication No. EP 602 863. The disclosures of each of these documents is incorporated herein by reference in their entirety.

[0053] The number average molecular weight of the polyalkylene tail in the polyalkylene succinic anhydride should be from about 300 to about 5000. This should be compatible with the previous ranges given before with the particular molecular weight depending on dispersant or mixture of dispersants to be employed. Preferably, the polyalkylene succinic anhydride component comprises from 2 to 40 weight percent, more preferably 10 to 15 weight percent of the weight of the lubricant composition.

[0054] Most preferable is the case where the polyalkylene succinic anhydride component is a polyisobutenyl succinic anhydride.

[0055] This invention is based, in part, on the discovery that the presently employed non-nitrogen containing polyalkylene succinic anhydrides and derivatives thereof provide significantly better water tolerance and compatibility than the use of conventional polyalkylene succinimides, such as polyisobutenyl succinimides, in lubricating compositions comprising an alkali metal borate. It has also been found that a mixture of polyalkylene succinic anhydrides can be effectively employed. The mixture preferably comprises a low molecular weight polyalkylene succinic anhydride component and a high molecular weight polyalkylene succinic anhydride component. Alternatively, various molecular weights polyalkylene succinic anhydride components can be combined as a dispersant.

[0056] The Detergent

[0057] There are a number of materials that are suitable as detergents for the purpose of this invention. These materials include phenates (high overbased or low overbased), high overbased phenate stearates, phenolates, salicylates, and sulfonates. Preferably, sulfonates are used, such as high overbased sulfonates, low overbased sulfonates, or phenoxy sulfonates. In addition the sulfonic acids themselves can also be used.

[0058] The term "metal sulfonate" is intended to encompass the salts of sulfonic acids derived from petroleum products. Such acids are well known in the art. They can be obtained by treating petroleum products with sulfuric acid or sulfur trioxide. The acids thus obtained are known as petroleum sulfonic acids and the salts as petroleum sulfonates. Most of the compounds in the petroleum product which become sulfonated contain an oil-solubilizing group. Also included within the meaning of sulfonates are the salts of sulfonic acids of synthetic alkyl aryl compounds. These acids also are prepared by treating an alkyl aryl compound with sulfuric acid or sulfur trioxide. At least one alkyl substituent of the aryl ring is an oil-solubilizing group. The acids thus obtained are known as alkyl aryl sulfonic acids and the salts as alkyl aryl sulfonates. The sulfonates wherein the alkyl is straight-chain are the well-known linear alkyl sulfonates.

[0059] The acids obtained by sulfonation are converted to the metal salts by neutralizing with a basic reacting alkali or alkaline earth metal compound to yield the Group I or Group II metal sulfonates. Generally, the acids are neutralized with an alkali metal base. Alkaline earth metal salts are obtained from the alkali metal salt by metathesis. Alternatively, the sulfonic acid can be neutralized directly with an alkaline earth metal base.

[0060] Alternatively, the sulfonic acid can be used directly, instead of the sulfonic acid salt.

[0061] Preferably, the metal sulfonate is a calcium alkyl aromatic sulfonate and the metal sulfonate comprises from 0 to 20 weight percent, more preferably 2 to 10 weight percent, of the lubricant composition.

[0062] The Oil of Lubricating Viscosity

[0063] The lubricating oil to which the borates and the dispersant are added can be any hydrocarbon-based lubricating oil or a synthetic base oil stock. The hydrocarbon-based lubricating oils may be derived from synthetic or natural sources and may be paraffinic, naphthetic or asphaltenic base, or mixtures thereof. The diluent oil can be natural or synthetic, and can be different viscosity grades.

[0064] The lubricating oil comprises from 30 to 70 weight percent, more preferably from 45 to 55 weight percent of the lubricant composition.

[0065] Formulations

[0066] The borate lubricating compositions of the present invention are generally blended at a level of 20-80% with other conventional additives such as ashless dispersants (1-20%), sulfurized hydrocarbons (0-30%), dialkyl hydrogen phosphates (0-10%), zinc dithiophosphates (0-20%), dialkyl hydrogen phosphates (0-10%), pentaerythritol monooleate (0-10%), 2,5-dimercapto thiadiazole (0-5%), benzotriazole (0-5%), dispersed molybdenum disulfide (0-5%), overbased sulfonates (0-10%), imidazolines (0-10%), and the like. Such additive mixtures can be used to provide a gear oil package which can then be blended at 5-15% level in an oil of lubricating viscosity, along with a polymethacrylate viscosity index improver at a level of 2-12%, and 0-1% pour point depressant to form a gear oil finished oil.

[0067] A variety of other additives can be present in lubricating oils of the present invention. Those additives include antioxidants, other viscosity index improvers, rust inhibitors, corrosion inhibitors, other anti-wear agents, and a variety of other well-known additives.

EXAMPLES

[0068] The invention will be further illustrated by the following examples, which set forth particularly advantageous method embodiments. While the Examples are provided to illustrate the present invention, they are not intended to limit it.

[0069] As used herein, the following abbreviations have the following meanings. If not defined, the abbreviation will have its art recognized meaning.

cSt =	centistokes
g =	gram
LOB =	low overbased
M =	metal
mm =	millimeters
mL =	milliliter
Mn or M_n =	number average molecular weight
PIB =	polyisobutylene
PIBSA =	polyisobutenyl succinic anhydride
PSD =	particle size distribution

-continued

TBN =	total base number
vis =	viscosity

COMPARATIVE EXAMPLE A

Preparation of the Lubricant Composition Using Nitrogen Containing Succinimides

[0070] To a 2-liter beaker were added 272.8 grams of water, 219.6 grams of boric acid (3.55 moles), and 148.3 grams of 45% potassium hydroxide solution (1.19 moles). The potassium hydroxide solution typically contained about 2% potassium carbonate. The alkali metal/boron charge mole ratio was 1:3. This was heated with stirring until the ingredients dissolved. Then this solution was divided in half and then each half, 594 grams, was added to a mixture of a mono tetraethylenepentamine succinimide made from 950 molecular weight PIB (polyisobutene) (30.25 grams), and a low overbased 5 TBN calcium natural sulfonate (13.15 grams) dissolved in 136.15 grams neutral diluent oil. The dispersant/boric acid weight ratio was 0.276:1, and the sulfonate/boric acid weight ratio was 0.121:1.

[0071] The two solutions were stirred rapidly for thirty minutes using Waring blenders and then poured together into a 2-liter beaker. This solution was then stirred and heated to 270° C. under a stream of nitrogen. Then it was allowed to cool. A total of about 561 grams product was produced. This product was found to contain a total base number of 122 mg KOH/g sample, 6.8% K, 5.9% B, 0.24% N, and had a vis at 100° C. of 15.9 cSt. The PSD (particle size distribution) was 90% less than 0.42 micron, and 50% less than 0.33 micron. This data is shown in Table 1.

COMPARATIVE EXAMPLES B-D

Preparation of Other Lubricant Compositions Using Different Amounts of Succinimide and Sulfonate

[0072] A number of other examples of lubricant compositions were prepared using the procedure outlined above with different amounts of the dispersant and the detergent. Comparative example B did not use a dispersant while comparative example C did not use a sulfonate. Comparative example D also used sodium hydroxide instead of potassium hydroxide. The sodium hydroxide typically contained about 0.6% sodium carbonate. These are also summarized in Table 1.

EXAMPLE 1

Preparation of the Lubricant Composition Using PIBSA as the Dispersant

[0073] To a beaker was added water, boric acid, and potassium hydroxide. The potassium to boron molar ratio was 0.33:1. This was heated until the boric acid dissolved. Then this was slowly added to a vigorously stirred solution of PIBSA made from polyisobutene that had a number average molecular weight of 1000 and a low overbased 5 TBN calcium natural sulfonate, dissolved in neutral diluent oil. This was stirred for one half hour, the mixture was heated with stirring until the temperature increased to 270°

F. The excess water was removed with a stream of nitrogen gas during the heating stage. The levels of dispersant and sulfonate, and chemical and physical properties of this product are reported in Table 1.

EXAMPLES 2-16

Preparation of Other Lubricant Compositions

[0074] Other lubricant compositions were prepared using the general procedure of Example 1. Different amounts of polyisobutenyl succinic anhydrides made from different molecular weight polyisobutenes, as well as mixtures of molecular weight polysiobuentenes, were used in these preparations. Also in some cases sodium hydroxide was used instead of potassium hydroxide. The sodium hydroxide employed typically contained about 0.6% sodium carbonate. Furthermore, examples 14-16, employed a calcium low overbased 28 TBN synthetic sulfonate, i.e., calcium alkylbenzene sulfonate, in place of the low overbased calcium natural sulfonate. These results are summarized in Table 1.

TABLE 1

Chemical and Physical Properties of the Borate Dispersions.

Ex.	M	PIB Mn	Dispersant Level	Sulfonate Level	TBN	% M	% B	% N	Vis.	PSD 90%	PDS 50%
			Dispersant - succinimide; sulfonate - natural sulfonate								
A	K	1000	11%	5%	122	6.8	5.9	0.24	15.9	0.42	0.33
B	K	—	—	5.3%	129	9.0	7.3	0.15	9.1	0.58	0.38
C	K	1000	11%	—	129	8.5	6.9	0.26	12.4	0.53	0.33
D	Na	1000	11%	5%	129	4.3	5.9	0.29	14.1	0.37	0.32
			Dispersant - polyalkylene succinic anhydride; sulfonate - natural sulfonate								
1	K	1000	11%	5%	115	6.7	6.4	—	18.9	0.60	0.34
2	K	1300	11%	5%	118	6.7	6.4	—	21.7	0.52	0.33
3	K	2300	11%	5%	118	6.9	6.1	—	20.0	0.60	0.38
4	K	1000	11.3%	—	123	7.0	6.7	—	17.3	0.58	0.35
5	K	1300	11.3%	—	124	6.8	6.4	—	21.6	0.59	0.35
6	K	2300	11.3%	—	108	6.0	5.3	—	15.8	1.50	0.40
7	Na	1000	11%	5%	121	4.8	6.8	—	17.5	0.57	0.34
8	Na	1300	11%	5%	123	4.5	6.7	—	20.3	0.47	0.32
9	Na	2300	16.7%	4.4%	114	4.3	6.1	—	27.0	0.57	0.35
10	Na	1000	11.3%	—	129	4.9	6.9	—	16.0	0.63	0.36
11	Na	1300	11.3%	—	129	4.6	7.0	—	18.9	0.54	0.34
12	Na	2300	16.7%	—	120	4.3	6.1	—	24.1	0.63	0.36
13	Na	1000 + 2300	17.6%	—	121	4.2	6.3	—		0.17	0.13
			Dispersant - polyalkylene succinic anhydride; sulfonate - synthetic sulfonate								
14	Na	1000	11%	5%	123	4.2	6.6	—		0.19	0.15
15	Na	500 + 1000 + 2300	11%	5%	121	4.6	6.3	—		0.17	0.13
16	Na	1000 + 2300	11%	5%	120	5.0	6.6	—		0.17	0.13

[0075] Compatibility Testing of the Borate Lubricating Composition

[0076] The compatibility testing of a number of borate lubricating compositions in the absence of water was carried out at 80° C. This was carried out by the following procedure. Borate lubricating compositions of the present invention were blended at 3% level into a typical automotive gear oil formulation comprising ashless dispersant, calcium sulfonate, corrosion inhibitor, EP agent, friction modifier, multifunctional additives, metal deactivator, etc. This gear oil formulation was then added at the level of 6.5% to diluent oil to make an 80W90 formulation. This formulation was then placed in an oven at 60° C. and inspected on a regular basis. The results are reported in Table 2.

TABLE 2

Compatibility of Borate Lubricating Compositions at 60° C.

Ex.	1 day	1 week	2 weeks	1 month
	Compatibility Results			
A	Slightly cloudy no sediment	Bright heavy sediment (15 mm)	Bright heavy sediment (10 mm)	Bright heavy sediment (10 mm)
D	Bright very heavy sediment (5 mm)	Bright very heavy sediment (5 mm)	Bright heavy sediment (6 mm)	
7	Bright no sediment	Bright no sediment	Very slight cloud no sediment	Very slight cloud no sediment

TABLE 2-continued

Compatibility of Borate Lubricating Compositions at 60° C.

Ex.	1 day	1 week	2 weeks	1 month
	Compatibility Results			
8	Bright no sediment	Bright no sediment	Bright no sediment	Bright no sediment

TABLE 2-continued

Compatibility of Borate Lubricating Compositions at 60° C.

Ex.	Compatibility Results 1 day	1 week	2 weeks	1 month
11	Bright no sediment	Bright no sediment	Very slight cloud no sediment	Very slight cloud no sediment
12	Bright no sediment	Bright no sediment	Very slight cloud no sediment	Very slight cloud no sediment
13	Bright no sediment	Bright no sediment	Bright no sediment	Bright no sediment
16	Bright no sediment	Bright no sediment	Bright no sediment	Bright no sediment

[0077] These results show that the borate lubricating compositions that used the PIBSA and mixtures of PIBSA's gave better performance (less sediment) than the borate lubricating compositions that used the succinimides.

[0078] Water Tolerance Data for Borates

[0079] In order to measure and quantify the water tolerance and compatibility properties of the borate lubricating compositions of this invention, we ran the following procedures listed below.

[0080] In the first procedure, we first blended the borate lubricating compositions of the present invention at the 3% level into a typical automotive gear oil formulation comprising, ashless dispersant, calcium sulfonate, corrosion inhibitor, EP agent, friction modifier, multifunctional additives, metal deactivator, etc. This gear oil formulation was then added at the level of 6.5% to diluent oil to make an 80W90 formulation. This formulation was then run in a modified L60 test. This test is a standardized test described in the ASTM Special Technical Publication 512A, "Laboratory Performance Tests for Automotive Gear Lubricants Intended for API GL-5 Service STP 512A". This information is available from ASTM, 1916 Race Street, Philadelphia, Pa. 19103. We modified the L60 test by omitting the copper coupon, eliminating air bubbling, and plugging the air holes in the gear case assembly. The gear case assembly was charged with 360 mL oil, and kept at 297° F. for 100 minutes. Then the oil was cooled to 175° F. and 3% water was added. Then the gear case assembly was held at 175° F. for 12 hours and then the temperature was increased to 275° F. The oil was kept at 275° F. for 12 hours, then the oil was drained. After draining the oil, the deposits were collected, measured, and reported in milliliters. The collected deposits were rinsed with hexane to remove the oily part, and then the deposits were measured again and reported in milliliters. The results from the water tolerance testing of a number of borate additives are shown in Table 3.

TABLE 3

Water Tolerance Testing for Borate Lubricating Compositions Using a Modified L60 Test

Ex.	Metal	Dispersant	Detergent	Deposits before hexane	Deposits after hexane
A	K	Succinimide	Sulfonate A	3.4	3.4
B	K	None	Sulfonate A	6.6	0.3
C	K	Succinimide	None	16.2	1.2
D	Na	Succinimide	Sulfonate A	0.1	0
1	K	PIBSA (1000)	Sulfonate A	17.6	0.4
2	K	PIBSA (1300)	Sulfonate A	10.2	0.5
3	K	PIBSA (2300)	Sulfonate A	6.0	0.8
4	K	PIBSA (1000)	None	5.2	1.6
5	K	PIBSA (1300)	None	3.6	2.4
6	K	PIBSA (2300)	None	4.6	1.8
9	Na	PIBSA (2300)	Sulfonate A	0.4	0
10	Na	PIBSA (1000)	None	1.2	1.2
12	Na	PIBSA (2300)	None	0	0

Sulfonate A = Calcium low overbased 5 TBN natural sulfonate

[0081] The data in Table 3 shows that better water tolerance (lower amount of deposits) was observed when the metal used in the borate lubricating composition was sodium compared to potassium.

[0082] Additional water tolerance data for the borate lubricating compositions was obtained by the following procedure. We first blended the borate lubricating compositions of the present invention at the 3% level into a typical automotive gear oil formulation comprising, ashless dispersant, calcium sulfonate, corrosion inhibitor, EP agent, friction modifier, multifunctional additives, metal deactivator, etc. This gear oil formulation was then added at the level of 6.5% to diluent oil to make an 80W90 formulation. Then a mixture of the finished oil and 0.5 weight percent water was placed in an oven that was held at a temperature of 60° C. This was inspected for compatibility. The results of this study are shown in Table 4.

TABLE 4

Water Tolerance Results for Borate Lubricating Compositions with 0.5% Water at 60° C.

Ex.	Compatibility Results 1 day	5 days	1 week	2 weeks
A	Very slight cloudy heavy sediment (4 mm)	Bright heavy sediment (4 mm)	Bright heavy sediment (4 mm)	Bright heavy sediment (5 mm)
D	Bright slight sediment (1 mm)	Bright slight sediment (1 mm)	Bright slight sediment (1 mm)	Bright slight sediment (1 mm)
7	Medium moderate cloud no sediment	Medium moderate cloud very slight sediment	Medium moderate cloud slight sediment (1 mm)	Medium moderate cloud slight sediment (1 mm)
8	Medium moderate cloud no sediment	Medium moderate cloud very slight sediment	Medium moderate cloud slight sediment (2 mm)	Medium moderate cloud slight sediment (3 mm)
11	Medium moderate cloud no sediment	Medium moderate cloud very slight sediment	Medium moderate cloud slight sediment (1 mm)	Medium moderate cloud slight sediment (2 mm)

TABLE 4-continued

Water Tolerance Results for Borate Lubricating Compositions with 0.5% Water at 60° C.

	Compatibility Results			
Ex.	1 day	5 days	1 week	2 weeks
12	Moderate cloud no sediment	Moderate cloud no sediment	Medium moderate cloud very slight sediment	Medium moderate cloud very slight sediment
13	Flock no sediment	Flock no sediment	Flock no sediment	Flock · no sediment

[0083] These results show that the borate lubricating compositions that used the PIBSA and mixtures of PIBSA gave better performance (less sediment) than the borate lubricating compositions that used the succinimides.

[0084] Additionally the water tolerance and performance of lubricant compositions comprising a mixture of polyalkylene succinic anhydrides was evaluated. Specifically, the lubricant composition of this example employs a mixture of PIBSA's made from 1000 and 2300 M_n PIB (polyisobutene). Otherwise, this composition was identical to that of Example 11 above which is a borate prepared from a PIBSA made from a 1300 molecular weight PIB. The data for this composition as compared to that of Example 11 is shown in Table 5 below. The Coordinating Research Counsel L-33 test was used for testing and evaluating rust and corrosion inhibiting properties of the compounds of this invention, see U.S. Pat. No. 4,089,790 incorporated herein by reference. This test utilizes the compounds of interest in a bench mounted automotive differential assembly adding water to simulate a severe service in which corrosion promoting moisture in the form of condensed water vapor has accumulated in the axle assembly.

TABLE 5

Water Tolerance Performance of Sodium Borates Prepared from Mixtures of PIBSA

Ex.	PIB M_n	Metal	L-33 % deposits
11	1300	Na	2
13	1000 + 2300	Na	3
13	1000 + 2300	Na	9
13	1000 + 2300	Na	4
13	1000 + 2300	Na	4

[0085] These results indicate that the composition of Example 13 performs substantially as well as that of Example 11. Other mixtures of different molecular weights are anticipated to behave with similar results.

[0086] The performance of lubricant compositions comprising an alkali metal borate, a polyalkylene succinic anhydride and different LOB sulfonates (Examples 7 and 14) as well as lubricant compositions comprising an alkali metal borate, a mixture of molecular weight polyalkylene succinic anhydrides employing a LOB sulfonate (Examples 15 and 16). Specifically, the lubricant compositions of this comparison employ a mixture of PIBSA's made from either 500+1000+2300 M_n PIB or 1000+2300 M_n PIB and LOB sulfonate A and are compared to compositions employing a 1000 M_n PIB and LOB sulfonates A or B. Formulations and physical property data for Examples 7, and 14-16 were previously shown in Table 1. These borate lubricating compositions were blended at the 3% level into a typical automotive gear oil formulation comprising, ashless dispersant, calcium sulfonate, corrosion inhibitor, EP agent, friction modifier, multifunctional additives, metal deactivator, etc. This gear oil formulation was then added at the level of 6.5% to diluent oil to make an 80W90 formulation. The data for these compositions as compared to that of Examples 7 and 14 are shown in Table 6 below.

TABLE 6

Water Tolerance Performance of Sodium Borates Prepared from Mixtures of PIBSA plus a LOB sulfonate.

Ex. No.	PIB M_n	LOB Sulfonate	Metal	OH:B Ratio	L-33 % deposits
Ex. 7	1000	A	Na	1.01:1	2
Ex. 7	1000	A	Na	0.90:1	4
Ex. 14	1000	B	Na	0.85:1	3
Ex. 14	1000	B	Na	0.85:1	14
Ex. 15	500 + 1000 + 2300	B	Na	1.10:1	2
Ex. 15	500 + 1000 + 2300	B	Na	1.10:1	2
Ex. 16	1000 + 2300	B	Na	1.01:1	2
Ex. 16	1000 + 2300	B	Na	1.06:1	4
Ex. 16	1000 + 2300	B	Na	1.06:1	6

LOB Sulfonate A = Calcium low overbased 5 TBN natural sulfonate
LOB Sulfonate B = Calcium low overbased 28 TBN synthetic sulfonate

[0087] The data in Table 6 shows that the lubricant compositions employing a mixture of PIBSA's plus a LOB sulfonate perform equally as well as the borate prepared from a single PIBSA plus a LOB sulfonate.

EXAMPLES 17-23

Preparation of Borates That Contain Oxo Anions

[0088] The procedure for Example A was followed exactly except that different amounts (based on boric acid) of different oxo anions were added to the water solution of the boric acid and alkali metal hydroxide. The chemical and physical properties of these materials are shown in Table 7.

TABLE 7

Chemical and Physical Properties that include Oxo Anions

Ex	Metal	Oxo anion	% anion	TBN	% M	% B	% N	vis	PSD 90%	PSD 50%
17	K	Na_2MoO_3	3	143	8.4	6.5	0.29	16.8	0.59	0.32
18	K	Na_2SO_4	3	130	8.3	6.9	0.29	13.9	0.58	0.35
19	K	Na_2WO_3	1	130	8.5	6.7	0.22	14.3	0.54	0.34
20	K	Na_2SO_4 + Na_3PO_4	3+ 3	153	7.9	6.2	0.44	15.0	0.57	0.35
21	K	Na_4SiO_4	3	210	9.6	3.9	0.19	16.2	0.51	0.34
22	Na	Na_2SO_4	3	140	5.4	6.8	0.25	—	0.46	0.32
23	K	$NaNO_3$	3	132	8.2	6.6	0.52	15.7	0.38	0.31

[0089] In Table 7, the column "PSD 90%" refers to particle size distribution and is a measure of particle size wherein at least 90% of the particles are less than the indicated value, in microns. Similarly, the column "PSD 50%" measures particle size wherein at least 50% of the particles are less than the indicated value, in microns.

[0090] While the present invention has been described with reference to specific embodiments, this application is intended to cover those various changes and substitutions that may be made by those skilled in the art without departing from the spirit and scope of the appended claims.

What is claimed is:

1. A lubricant composition which comprises:

a) a base oil of lubricating viscosity,

b) a dispersed hydrated alkali metal borate, and

c) a dispersant that is selected from the group consisting of a polyalkylene succinic anhydride, a non-nitrogen containing derivative of the polyalkylene succinic anhydride, mixtures of polyalkylene succinic anhydrides, mixtures of non-nitrogen containing derivatives of the polyalkylene succinic anhydride and mixtures of both polyalkylene succinic anhydrides and non-nitrogen containing derivatives of the polyalkylene succinic anhydride.

2. The lubricant composition according to claim 1, wherein the dispersed hydrated alkali metal borate is a dispersed hydrated sodium borate.

3. The lubricant composition according to claim 2, wherein the dispersed hydrated sodium borate has a sodium to boron metal ratio of from about 1:2.5 to about 1:4.5.

4. The lubricant composition according to claim 1, wherein the dispersant is a mixture of polyalkylene succinic anhydrides.

5. The lubricant composition according to claim 4, wherein the mixture of polyalkylene succinic anhydrides is a mixture of polyisobutenyl succinic anhydrides.

6. The lubricant composition according to claim 5, wherein the mixture of polyisobutenyl succinic anhydrides comprises a low molecular weight polyisobutenyl succinic anhydride component and a high molecular weight polyisobutenyl succinic anhydride component.

7. The lubricant composition according to claim 6, wherein the low molecular weight polyisobutenyl succinic anhydride component has a number average molecular weight of from about 500 to below 1000 and the high molecular weight polyisobutenyl succinic anhydride component has a number average molecular weight of from 1000 to about 3000.

8. The lubricant composition according to claim 1, wherein the dispersed hydrated alkali metal borate has a ratio of at least 2:1 relative to the dispersant.

9. The lubricant composition according to claim 8, wherein the dispersed hydrated alkali metal borate has a ratio of from 2:1 to 10:1 relative to the dispersant.

10. The lubricant composition according to claim 8, wherein the dispersed hydrated alkali metal borate has a ratio of at least 5:2 relative to the dispersant.

11. The lubricant composition according to claim 1, which further comprises a metal sulfonate.

12. The lubricant composition according to claim 11, wherein said metal sulfonate is a calcium alkyl aromatic sulfonate.

13. The lubricant composition according to claim 1, which further comprises from about 0.001 moles to about 0.11 moles of a water soluble oxo anion per mole of boron.

14. The lubricant composition according to claim 13, wherein said oxo anion is selected from the group consisting of nitrate, sulfate, carbonate, phosphate, pyrophosphate, silicate, aluminate, germanate, stannate, zincate, plumbate, titanate, molybdate, tungstate, vanadate, niobate, tantalate, uranate, isopolymolybdate, isopolytungstate, heteropolymolybdate, heteropolytungstates, and mixtures thereof.

15. A method for enhancing the water tolerance of lubricant compositions comprising alkali metal borate which method comprises adding an anti-wear effective amount of a dispersed hydrated alkali metal borate to a base oil of lubricating viscosity in combination with a dispersant effective amount of a dispersant selected from the group consisting of a polyalkylene succinic anhydride, a non-nitrogen containing derivative of the polyalkylene succinic anhydride, mixtures of polyalkylene succinic anhydrides, mixtures of non-nitrogen containing derivatives of the polyalkylene succinic anhydride and mixtures of both polyalkylene succinic anhydrides and non-nitrogen containing derivatives of the polyalkylene succinic anhydride.

16. The lubricant composition according to claim 1, wherein the dispersed hydrated alkali metal borate is a dispersed hydrated sodium borate having a hydroxyl to boron ratio of from about 0.8:1 to 1.6:1.

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MOLYBDENUM COMPOUNDS

The chemistry of molybdenum, Mo, is among the most diverse of the transition elements. In its compounds, molybdenum exhibits coordination numbers from four to eight, oxidation numbers from −II to VI, and numerous states of aggregation (nuclearity). Molybdenum forms binary compounds with many nonmetallic elements, and a number of these, namely the halides, oxides, sulfides, carbides, nitrides, and silicides, are of technological interest. In contrast to its congeners, chromium and tungsten, molybdenum is found naturally in the form of its sulfide molybdenite [*1309-56-4*], MoS_2. Similarly, in the enzymes in which molybdenum is found, the active site Mo is generally in a high sulfur environment. This thiophilicity of Mo also plays a role in a number of its technological uses.

In biology molybdenum is a component of fertilizer and nutrient formulations (see FERTILIZERS; MINERAL NUTRIENTS). Over 20 enzymes have been found to have molybdenum as a component of their active sites. The roles of molybdenum in nitrogen fixation (qv) and nitrate reduction establish this metal as a key element of a biological nitrogen cycle. In technology various solid and soluble molybdenum compounds have found use in lubrication (see LUBRICATION AND LUBRICANTS); hydrodesulfurization, hydrogenation, and oxidation catalysis; anticorrosion and coatings (qv); flame and smoke retardancy (see FLAME RETARDANTS); and various forms of pigmentation.

The most important molybdenum oxidation states are VI, V, IV, III, II, and 0. The higher oxidation states are usually characterized by molybdenum binding to electronegative atoms, such as oxygen and the halogens. The lowest oxidation states are largely in the realm of organometallic chemistry, wherein the Mo is bound directly to the carbon atom of carbon monoxide (qv), to organic phosphines, and/or to a variety of unsaturated carbonaceous ligands.

Molybdenum(VI)

The chemistry of hexavalent molybdenum is very prominent in both biological and industrial systems. Oxygen coordination of molybdenum is most common in this oxidation state (1–3). Molybdenum trioxide [*1313-27-5*], MoO_3, is a key intermediate in the technological utilization of molybdenum (Fig. 1). In the refining of Mo, molybdenite ore, MoS_2, which contains tetravalent Mo, is first roasted in air to form impure MoO_3. The MoO_3 is then reduced to the metal with hydrogen from 500–1150°C. The trioxide melts at 795°C but sublimes significantly below that temperature. The structure of MoO_3 is a complex, layered arrangement in which each of the six-coordinate Mo(VI) atoms shares the face of an octahedron with another Mo(VI) atom. The MoO_3 reacts with base to produce a variety of molybdate salts, the simplest of which are of the form M_2MoO_4. Sodium molybdate [*7631-95-0*] is an example. These water-soluble salts serve as the starting materials for the synthesis of a wide variety of compounds.

The molybdate ion, MoO_4^{2-}, is a d^0, four-coordinate, tetrahedral anion. The structure (Fig. 2a) resembles that of other Group 6 (VIB) and Group 16 (VIA) ions, such as CrO_4^{2-}, WO_4^{2-}, SO_4^{2-}, and SeO_4^{2-}. The discrete dimolybdate ion [*19282-23-6*], $Mo_2O_7^{2-}$, exists in $N(C_4H_9)_4^+$ salts (see QUATERNARY AMMONIUM

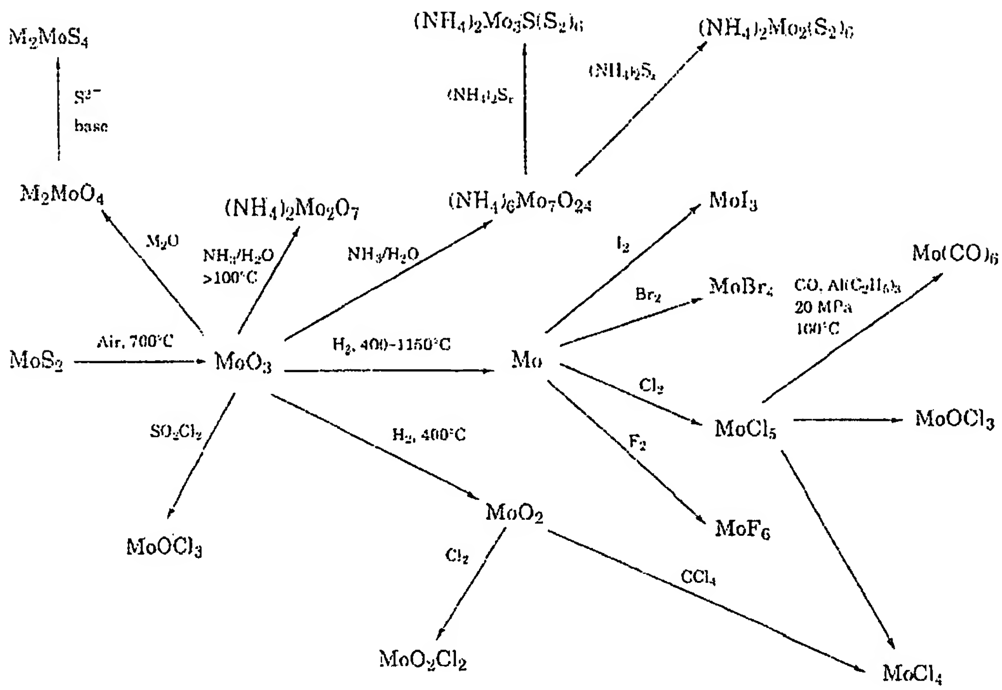

Fig. 1. Scheme for the preparation of technologically important compounds of molybdenum, where M = Li, Na, K, Rb, Cs, and NH_4. To convert MPa to psi, multiply by 145.

COMPOUNDS). Diammonium dimolybdate [*27546-07-2*], $(NH_4)_2Mo_2O_7$, available commercially as the tetrahydrate and prepared from MoO_3 and excess NH_3 in aqueous solution at 100°C, has an infinite chain structure based on MoO_6 octahedra. In aqueous solution the behavior of Mo(VI) is extremely pH-dependent (4). Above pH 7 molybdenum(VI) occurs as the tetrahedral oxyanion MoO_4^{2-}, but below pH 7 a complex series of concentration-, temperature-, and pH-dependent equilibria exist. The best known of these equilibria lead to the formation of the heptamolybdate, $Mo_7O_{24}^{6-}$ (Fig. 2h), and octamolybdate, $Mo_8O_{26}^{4-}$, ions. Even larger aggregates may be present in solution and in salts. Both $Mo_{12}O_{37}^{2-}$ and $Mo_{36}O_{112}(H_2O)_{16}^{8-}$ have been isolated and crystallographically characterized (4). At sufficiently low pH in very dilute solutions, cationic forms such as MoO_2^{2+} and MoO^{4+} are present.

The polymolybdate and heteropolymolybdate ions constitute a broad and commercially significant class. In these ions molybdenum is six-coordinate with octahedral geometry (4–8). Oxo (O^{2-}) groups bridge the Mo atoms and serve as terminal ligands on some of the Mo ions. When other atoms are present during the acidification of molybdate solutions, a series of heteropolymolybdates is formed. For example, cations such as Cr^{3+} or Co^{2+}, or anions such as PO_4^{3-} or AsO_4^{3-}, form the heteropoly anions $H_6CrMo_6O_{24}^{3-}$, $H_6CoMo_6O_{24}^{4-}$, $PMo_{12}O_{40}^{3-}$, and $AsMo_{12}O_{40}^{3-}$, respectively. The yellow ion, $PMo_{12}O_{40}^{3-}$, is analytically useful, being formed in the molybdenum test for phosphate ion. Poly- and heteropolymolybdate ions are used in the precipitation of dyes. The protonated forms of the ions are strongly acidic and many poly- and heteropolymolybdate

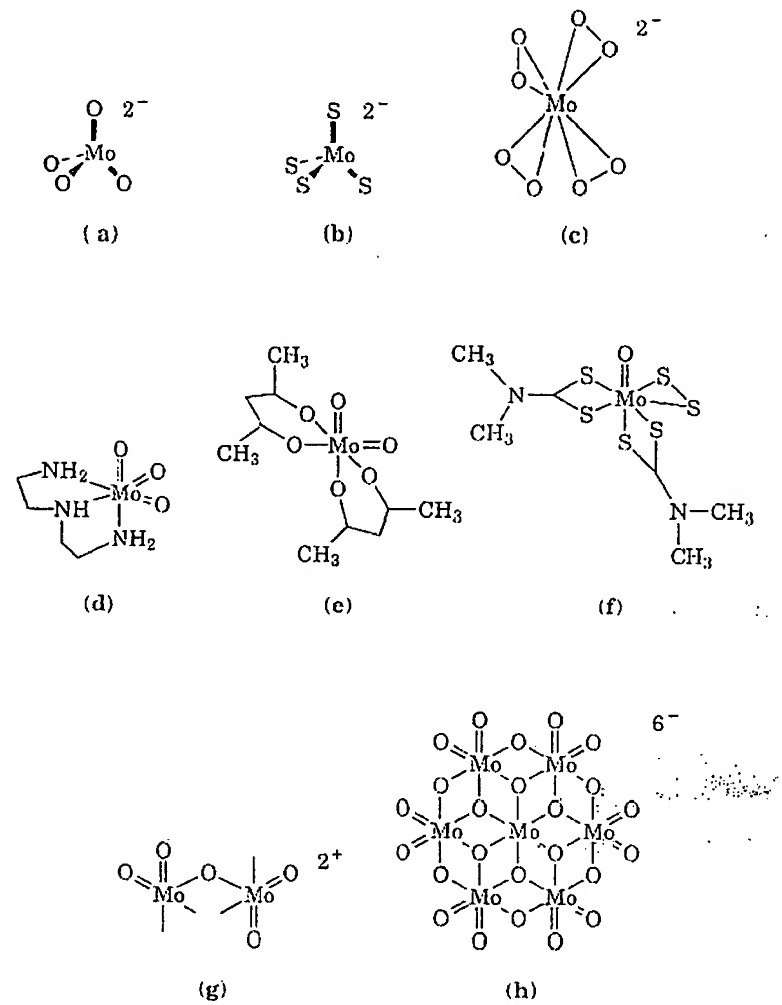

Fig. 2. Representative structures for compounds of molybdenum(VI): (a) molybdate(VI), MoO_4^{2-}; (b) tetrathiomolybdate(VI), MoS_4^{2-}; (c) tetrakis(peroxo)molybdate(VI), $Mo(O_2)_4^{2-}$; (d) *cis*-trioxodiethylenetriaminemolybdenum(VI), (MoO_3(dien)), $C_4H_{13}N_3MoO_3$; (e) *cis*-bis(acetylacetonato)dioxomolybdenum(VI), $MoO_2(C_5H_7O_2)_2$; (f) bis(dialkyldithiocarbamato)disulfidooxomolybdenum(VI), $MoO(S_2)(S_2CNR_2)_2$ (R = alkyl); (g) the dinuclear core structure for $Mo_2O_5^{2+}$ complexes; (h) heptamolybdate(VI), $Mo_7O_{24}^{6-}$.

compounds have catalytic activity that is attributable to their acid–base or redox properties.

The reduction of molybdate salts in acidic solutions leads to the formation of the molybdenum blues (9). Reductants include dithionite, stannous ion, hydrazine, and ascorbate. The molybdenum blues are mixed-valence compounds where the blue color presumably arises from the intervalence Mo(V) → Mo(VI) electronic transition. These can be viewed as intermediate members of the class of mixed oxy hydroxides the end members of which are Mo(VI)O_3 and Mo(V)O$(OH)_3$ [*27845-91-6*]. MoO_3 and Mo(VI) solutions have been used as effective detectors of reductants because formation of the blue color can

36.1

Molybdenum: The Element and Aqueous Solution Chemistry

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36.1.1 THE ELEMENT

Molybdenum occurs chiefly as molybdenite, MoS_2, but also as molybdates $PbMoO_4$ and $MgMoO_4$. The largest known deposits are in Colorado (USA), but it is also found in Canada and Chile. The natural abundance in the earth's crust (~1.2 p.p.m.) is about the same as that of tungsten, but is much less than of chromium (122 p.p.m.). The name in fact originates from the Greek *molybdos* meaning lead.

The Swedish chemist Scheele (1778) produced the oxide of a new element from (black) MoS_2, thereby distinguishing the element from graphite with which it had been confused. The metal was isolated by Hjelm in Sweden three to four years later by heating the oxide with charcoal. In the procedure now used to isolate the metal, the MoS_2 component in ores is concentrated by flotation methods. The concentrate is then converted by roasting into MoO_3, which, after purification, is reduced with hydrogen. Reduction with carbon is avoided since carbides rather than the metal are obtained.

The chief use of molybdenum is in steels. The oxides and sulfides have some applications as catalysts. Molybdenum is the only element in the second and third transition series which appears to have a major role as a trace metal in enzymes. Several aspects of molybdenum chemistry have been widely studied in order to gain a better understanding of the biological relevance. Molybdenum is one of the few elements which currently has its own series of international conferences.[1]

Molybdenum and tungsten are similar chemically, although there are differences which it is difficult to explain. There is much less similarity in comparisons with chromium. In addition to the variety of oxidation states there is a wide range of stereochemistries, and the chemistry is amongst the most complex of the transition elements.

36.1.2 AQUEOUS SOLUTION CHEMISTRY

36.1.2.1 General Introduction

Molybdenum has an extensive aqueous solution chemistry for oxidation states II through VI. It is unique in having aqua or aqua/oxo ions for all five states in acidic solution (pH < 2). These are well defined in all but the Mo^{VI} case, the study of which is complicated by the existence of rapid equilibria involving protonated/deprotonated monomer/dimer (and higher) forms. The VI state is without question the most stable and in contrast to Cr^{VI} is only the mildest of oxidants. Compounds which have contributed to the development of the aqueous solution chemistry, including the aqua ions themselves, are considered under Section 36.1.2. It is only since 1971 that the aqua forms of oxidation state II–V ions have been identified, and

preparative as well as structural features defined.[2] The chemistry of aqua ions generally has a somewhat elevated position, since they are often regarded as a point of reference or prototype for the behaviour of a particular oxidation state. Since they are difficult to crystallize, structures of derivative complexes are relevant. The simple aqua ions of oxidation states II–VI are indicated in Table 1. The quite different structures of adjacent oxidation states are to be noted, which gives rise to an interesting and varied redox chemistry. All but $[Mo(H_2O)_6]^{3+}$ are diamagnetic and metal–metal bonding is a significant contributing feature.

Table 1 Summary of Aqua Ions of Molybdenum at pH < 2

Description	*Formula*	*Mo—Mo bonding*	*Colour*
Mo_2^{II}	$[Mo_2(H_2O)_8]^{4+}$	Quadruple	Red
Mo^{III}	$[Mo(H_2O)_6]^{3+}$	None	Pale yellow
Mo_2^{III}	$[Mo_2(OH)_2(H_2O)_8]^{4+}$	Triple	Green
Mo_3^{IV}	$[Mo_3O_4(H_2O)_9]^{4+}$	Single	Red
Mo_2^{V}	$[Mo_2O_4(H_2O)_6]^{2+}$	Single	Yellow
Mo_x^{VI}	Different forms $x = 1$ and 2	None	Colourless

The three most often used 'lead in' compounds for the chemistry described are sodium molybdate, $Na_2[MoO_4]\cdot 2H_2O$, molybdenum hexacarbonyl, $[Mo(CO)_6]$, and potassium hexachloromolybdate, $K_3[MoCl_6]$. Synthesis of II and III state complexes generally requires rigorous O_2-free techniques, using a range of methods from those involving Schlenk apparatus to the use of N_2 or Ar gas, syringes, Teflon tubing and/or stainless steel needles, and rubber seals. In some cases solutions of IV and V state complexes must also be stored O_2 free. Perchlorate cannot be used with II and III aqua ions, and also appears to oxidize some trimeric Mo^{IV} ions on leaving overnight. Instead weakly coordinating, redox inactive and strongly acidic trifluoromethanesulfonic acid, CF_3SO_3H (abbreviated HTFMS or triflate), or p-toluenesulfonic acid, $C_6H_4(Me)SO_3H$ (abbreviated HPTS), finds wide usage. Methanesulfonic acid, $MeSO_3H$, has also been used.

36.1.2.2 Oxidation State II

The aqueous chemistry of the II state is dominated by dimeric complexes. The latter constitute the largest group of compounds of any element containing quadrupule bonds, a subject extensively covered in the Cotton and Walton text.[3] Soon after the recognition of the quadruple bond in $[Re_2Cl_8]^{2-}$ in 1964 the structure of $[Mo_2(O_2CMe)_4]$, Figure 1, was published (Mo—Mo distance 2.09 Å).[4] The $[Mo_2Cl_8]^{4-}$ complex, Figure 2, is obtained by treating $[Mo_2(O_2CMe)_4]$ in aqueous KCl solution with 12 M HCl at 0 °C when crystals of $K_4[Mo_2Cl_8]\cdot 2H_2O$ are obtained. Similarly the bromo analogue $(NH_4)_4[Mo_2Br_8]$ has been isolated. There are no bridging ligands and in both cases the Mo—Mo distance remains short (2.14 Å), consistent with retention of a quadruple metal–metal bond.[5] For comparison, typical M—M distances for quadruply bonded dimeric d^4 complexes are 2.21 Å (for $[W_2(O_2CCF_3)_4]$), 2.19 Å (for $[Tc_2(O_2CCMe_3)_4Cl_2]$)[7] and 2.2 Å (for $K_2[Re_2Cl_8]\cdot 2H_2O$).[3,4b] The d^4–d^4 technetium complex is the only Tc_2^{III} example for which there is structural information, and the ease with which $[Tc_2Cl_8]^{3-}$ rather than $[Tc_2Cl_8]^{2-}$ is obtained is at present puzzling. The range of metal–metal distances in Mo_2^{II} complexes (2.04–2.18 Å) is much smaller than that observed for Cr_2^{II} (1.83–2.54 Å).[3]

Examples of monomeric Mo^{II} complexes are much less common. It has been demonstrated that the $[Mo(CN)_7]^{5-}$ ion has a pentagonal bipyramidal structure. Other examples are nitrile (*i.e.* isocyanide) complexes $[Mo(CNR)_7]^{2+}$, which has a capped trigonal prismatic structure, and the diarsine complex $[Mo(diars)_2X_2]$.

The acetate complex $[Mo_2(O_2CMe)_4]$ is obtained by heating $[Mo(CO)_6]$ with glacial acetic acid or a mixture of the acid and its anhydride.[8] Yields are low (15–20%), but can be improved (~80%) when diglyme is used as solvent.[9] The low yields are the result of the formation of trinuclear Mo^{IV} complexes of the type $[Mo_3X_2(O_2CMe)_6(H_2O)_3]^{4+}$, where the Mo_3X_2 unit is a trigonal bipyramid with capping groups X either O or CMe (alkylidene).

$[Mo_2O_4^{2+}]$ consistent with a mechanism shown in equations (30) and (31). From EPR measurements it has been confirmed that mononuclear Mo^V is present.

$$Mo_2^V \rightleftharpoons 2Mo^V \tag{30}$$

$$Mo^V + NO_3^- \longrightarrow \text{products} \tag{31}$$

Pulse radiolysis studies on $[Mo_2O_4(edta)]^{2-}$, $[Mo_2O_2S_2(edta)]^{2-}$, $[Mo_2O_4(cys)_2]^{2-}$ and $[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-}$ at pH ~6, in which the Mo_2^V is reduced with e_{eq}^- and Zn^+ to the $Mo^{IV,V}$ mixed-valence form have been reported.[145] The latter absorbs in the visible range (ε 300–500 $M^{-1}\,cm^{-1}$ per dimer). In the absence of O_2 the decay is relatively slow ($t_{1/2}$ ~5–10 s), and does not result in Mo^{III} production. With O_2 present there is rapid (~$10^8\ M^{-1}\,s^{-1}$) oxidation back to Mo_2^V.

Inner-sphere paths are observed in the Cr^{2+} reduction of 10^{-4}–10^{-3} M solutions of Mo_2^V, $[Mo_2O_4(H_2O)_6]^{2+}$, and of Mo_3^{IV}, $[Mo_3O_4(H_2O)_9]^{4+}$, at 25 °C, $I = 2.0$ M (NaPTS).[146] In 1.9 M HPTS and with $[Cr^{2+}]$ in a greater than ten-fold excess of Mo_2^V, the reaction proceeds *via* a grey-green Cr-containing intermediate (~1 min), to give a product with the Mo_2^{III} spectrum (~24 h). The rate law for formation of the intermediate is of the form $k_1[Cr^{2+}]^2[Mo_2^V][H^+]$, with $k_1 = 9.1 \times 10^3\ M^{-3}\,s^{-1}$. Decay of the intermediate is independent of Cr^{2+} and can be expressed as k_2[intermediate]$[H^+]$. The rate constant $k_2 = 2.0 \times 10^{-5}\ M^{-1}\,s^{-1}$ is believed to correspond to a process involving loss of Cr^{III}. With a $Cr^{2+}:Mo_2^V$ ratio of reactants of 2:1 evidence for two intermediates is obtained (~1 min), one (green in colour) giving a Cr:Mo ratio of 1:1, and the other the same as that generated in the reaction of excess Cr^{2+} with Mo_2^V giving a Cr:Mo ratio of 2:1. Some 30% of the Mo remains as Mo_2^V. Over longer periods (~22 h) 60–70% overall conversion to Mo_3^{IV} is observed, and 24–30% of the Mo is present as Mo_2^V. In separate experiments, with Cr^{2+} in a greater than ten-fold excess, Mo_3^{IV} is reduced to $Mo^{III,III,IV}$ in a two-stage process, complete within 1 min, and then through to Mo_3^{III} (~40 min). Reduction of Mo_2^V to either Mo_2^{III} or Mo_3^{III} is observed therefore, depending on whether a single addition of excess Cr^{2+} or successive additions of Cr^{2+} are made.

36.1.2.6 Oxidation State VI

The solution chemistry of the Mo^{VI} state has been an area of intense research activity for several decades. It is dominated by the isopolymolybdate and heteropolymolybdate forms,[147] brief mention of which is included here. Such studies remain an active area of research with applications in the area of industrial catalysis.[1] More than 65 elements from all groups of the Periodic Table (except the rare gases) are implicated as heteroatoms in such structures.[147] In addition to the text by Pope,[147] a review of isopolyanions has appeared.[148] An overview on the hydrolysis of cations is also relevant.[149] At pH > 7 Mo^{VI} exists as the monomeric tetrahedral $[MoO_4]^{2-}$ ions. Polymers are generated by conversion of tetrahedral Mo^{VI} to octahedral forms in which there is edge, corner and (occasionally) face sharing of coordinated O^{2-} ions between adjacent Mo atoms. In the absence of heteropolyanions protonation to give $[HMoO_4]^-$, more precisely $[MoO_3(OH)]^-$ (pK_a 3.47 in 1 M HCl), is followed by a second protonation to give $[H_2MoO_4]$ (pK_a 3.7 in 1 M NaCl). The latter at least (possibly both) is believed to be octahedral and is sometimes referred to as $[Mo(OH)_6]$ although other formulations have been suggested.[150] The incidence of protonation at pH ~ 7 triggers polymerization. Polymeric forms play a dominant role in the chemistry of Mo^{VI} from pH 7 down to 2.[151] At pH 2 to 1 (depending on the concentration) break down of polymers to give dimeric and monomeric octahedral forms occurs, where the latter are often referred to as $[Mo(OH)_6]$. The first protonation constant for $[Mo(OH)_6]$ has been determined.[151b] Singly and doubly charged cationic species are present in such solutions,[151b,152] and formulae which have been suggested include *cis*-$[MoO_2(H_2O)_4]^{2+}$ and $[Mo(OH)_4(H_2O)_2]^{2+}$. The *cis*-dioxo structure is found in a number of mononuclear coordination complexes, including *cis*-$[MoO_2(Et_2dtc)_2]$ (Et_2dtc = *N,N*-diethyldithiocarbamate),[153] *cis*-$[MoO_2(tox)_2]$ (tox = thiooxine or 8-mercaptoquinolate),[154] Λ-*cis*-$[MoO_2\{(2R)\text{-cysOMe}\}_2]$ (cysOMe = l-cysteine methyl ester)[155] and Λ-*cis*-$[Mo_2(S)\text{-penOMe}_2]$ (penOMe = penicillamine methyl ester).[156] Two *cis* oxos are also present in the oxalato μ-oxo complex $[(H_2O)(C_2O_4)O_2MoOMoO_2(C_2O_4)(H_2O)]^{2-}$ (Figure 31).[157] Facial trioxo coordination is on the other hand present in $[MoO_3dien]$ (dien = diethylenetriamine)[158] and the ethylenediaminetetraacetate complex $[O_3Mo(edta)MoO_3]^{4-}$ [159] (Figure 32). Features of both structures are the MoO_3 bond angles (~106°) which are approaching those of a regular tetrahedron

and the Mo—O(oxo) bond lengths of ~1.74 Å which indicate a bond order of two. The bond angles N—Mo—N (75°) for the dien complex, and N—Mo—O (73°) and O—Mo—O (75°) for the edta complex also suggest that the structures should be regarded as pseudotetrahedral. From Raman studies[160] it has been concluded that $[MoO_3dien]$ is largely dissociated in water (equation 32), and reforms rapidly and quantitatively as a solid on addition of alcohol at pH ~7. Thus although it is necessary to replace an oxo ligand on $[MoO_4]^{2-}$ the reaction occurs rapidly.

$$[MoO_3dien] + H_2O \rightleftharpoons [MoO_4]^{2-} + dienH_2^{2+} \tag{32}$$

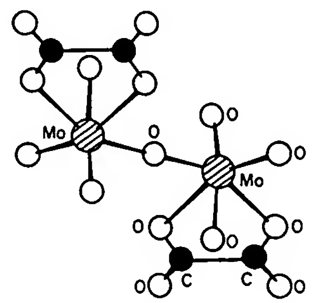

Figure 31 The structure of the Mo^{VI} complex $[Mo_2O_5(C_2O_4)_2(H_2O)_2]^{2-}$ [157]

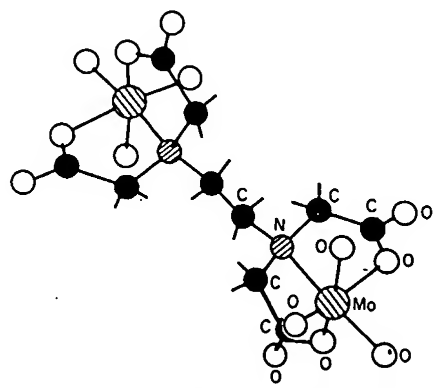

Figure 32 The structure of the Mo^{VI} complex $[O_3Mo(edta)MoO_3]^{4-}$ [159]

The polymeric forms obtained on decreasing the pH from 7 have been extensively investigated. For solutions with Mo^{VI} concentrations greater than 10^{-3} M, and pH in the range 3.0 to 5.5, the predominant form present is the heptamolybdate(VI) ion, $[Mo_7O_{24}]^{6-}$, sometimes referred to as paramolybdate (equation 33). Commercially available ammonium molybdate, $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$, is obtained by crystallization of a solution of MoO_3 in aqueous NH_3. In spite of numerous attempts, no intermediate has been unambiguously characterized in the aqueous conversion of $[MoO_4]^{2-}$ to $[Mo_7O_{24}]^{6-}$. At pH < 4 the β-$[Mo_8O_{26}]^{4-}$ octamolybdate form is obtained (equation 34). Representations of $[Mo_7O_{24}]^{6-}$ and $[Mo_8O_{26}]^{4-}$ are shown in Figure 33. The existence of significant amounts of the $[Mo_8O_{26}]^{4-}$ ion has been controversial, but recent Raman and X-ray scattering[161] studies would seem to provide confirmation of its existence. Previously the interpretation of EMF data (pH 2–3) has been uncertain, because equally acceptable fits are given by a series of protonated $[Mo_7O_{24}]^{6-}$ forms, as by a mixture of protonated $[Mo_7O_{24}]^{6-}$ and $[Mo_8O_{26}]^{4-}$. From one set of stability constant determinations, Figure 34 has been obtained, indicating the distribution of different species. The ditetrahedral $[Mo_2O_7]^{2-}$ ion has recently been identified in $Mg[Mo_2O_7]$ and in the double salt $K_2[Mo_2O_7],KCl$.[162,163] These structures are to be contrasted with the crystalline product $(NH_4)_2[Mo_2O_7]$, obtained from hot aqueous ammonium molybdate solution after some hours, which consists of infinite chains of tetrahedral MoO_4 and octahedral MoO_6 units.[164]

$$7[MoO_4]^{2-} + 8H^+ \rightleftharpoons [Mo_7O_{24}]^{6-} + 4H_2O \tag{33}$$

$$8[MoCl]^{2-} + 12H^+ \rightleftharpoons [Mo_8O_{26}]^{4-} + 6H_2O \tag{34}$$

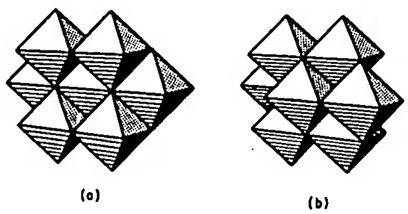

Figure 33 The structures of (a) heptamolybdate, $[Mo_2O_{24}]^{6-}$, and (b) octamolybdate, $[Mo_8O_{26}]^{4-}$ (one MoO_6 octahedron hidden)

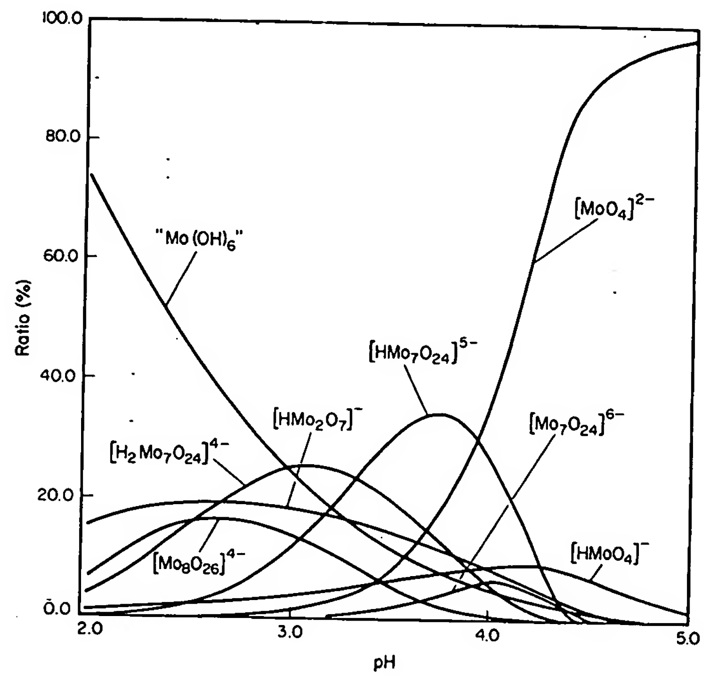

Figure 34 Distribution of Mo^{VI} forms with pH for a solution of 5×10^{-4} M molybdate at 25 °C, $I = 1.0$ M (NaCl), as calculated by A. Nagasawa and R. Iwata (unpublished work) from data in ref. 151

Solutions of Mo^{VI} acidified to $H^+/[MoO_4]^{2-} \sim 1.8$ contain one or more very large polymolybdate structures. Earlier measurements based on ultracentrifugation and EMF studies,[165] through to a recent structure report,[166] are consistent with a formula $[Mo_{36}O_{112}(H_2O)_{18}]^{8-}$. The reaction can be summarized as in equation (35). There are two seven-coordinate Mo^{VI} atoms in this structure. In all isopoly and heteropoly structures the metal ion does not lie at the centre of its polyhedron, but is displaced towards the exterior of the structure and towards a vortex or edge of its own polyhedron. Structures appear to be governed by electrostatic and radius-ratio principles as observed for extended ionic lattices. The Mo^{VI} tetrahedral radius is 0.55 Å (0.56 Å for W), the octahedral radius 0.73 Å (0.74 Å for W), and the radius of O^{2-} is 1.40 Å.[167]

$$36[MoO_4]^{2-} + 64H^+ \rightleftharpoons Mo_{36}O_{112}^{8-} + 32H_2O \quad (35)$$

Important differences are observed in comparing the behaviour of Mo^{VI} and W^{VI}. Equilibria involving $[MoO_4]^{2-}$ and polymolybdates in aqueous solution are established rapidly and are complete in a matter of minutes, whereas those for W^{VI} can take several weeks. The polyanions of tungsten are made up of WO_6 octahedra, but in other respects the behaviour of W^{VI} solutions is quite different, and structurally the polyanions in one series do not have precise counterparts in the other. Known structures of isopolytungstates from aqueous solution include $[W_4O_{16}]^{8-}$, $[W_4O_{19}]^{2-}$, $[W_{10}O_{32}]^{4-}$, $[H_2W_{12}O_{42}]^{10-}$ and $[H_2W_{12}O_{40}]^{6-}$.[147]

A number of other isopolymolybdate anions including $[Mo_6O_{19}]^{2}$, α-$[Mo_8O_{26}]^{4-}$ and $[Mo_5O_{17}H]^{3-}$ can be stabilized in non-aqueous or mixed solvents.[168] The $[Mo_2O_7]^{2-}$ ion is also obtained from acetonitrile solution. Tetrahedral coordination is retained in the latter.[169] There

are two distorted tetrahedra in α-$[Mo_8O_{26}]^{4-}$ above and below a crown of six octahedra formed by edge sharing. A tetrahedron spanning a ring of four edge- and face-shared octahedra is also believed to be present in $[Mo_5O_{17}H]^{3-}$.[170] The α and β structures can coexist in solution, and a cation dependent isomerization of α into β has been observed.[171]

Isopolymolybdates are generally colourless, and heteropoly forms can be coloured if another transition metal ion is present. Some other heteropolyanions can be coloured, for example that obtained by addition of ammonium molybdate to phosphoric acid to give ammonium 12-molybdophosphate, $[NH_4]_3[PMo_{12}O_{40}]$, which is yellow. The $[Mo_6O_{19}]^{2-}$ anion is unique for an isopolyanion in being yellow (λ_{max} 325 nm) and having a structure with a monocoordinated terminal oxo group rather than MoO_2 units. This ion is electrochemically reduced to the mixed valence $[Mo_6O_{19}]^{3-}$ and $[Mo_6O_{19}]^{4-}$ forms in DMF. Incorporation of the Mo^V state in blue-red and yellow mixed-valence species formulated as $[Mo_2^VMo_4^{VI}O_{18}]^{2-}$, $[Mo_3^VMo_3^{VI}O_{18}]^{2-}$ and $[Mo_2^VMo_4^{VI}O_{17}H]^{2-}$ respectively has also been reported. The reduction of addenda atoms in heteropolyanions results in the formation of heteropoly blues, and gives rise to a vast chemistry. The added electrons are delocalized according to varying timescales over certain atoms and/or regions of the structure.

Because the surfaces of polyanions have some similarities to those of metal oxides, it is thought they may have some relevance in the area of heterogeneous catalysis. As a result a whole new area concerned with the synthesis and study of organic and organometallic derivatives of polyanions is being investigated.[173]

A kinetic investigation of the ^{18}O exchange between water and molybdate $[MoO_4]^{2-}$ at pH > 11, $[OH^-] = 3 \times 10^{-3}$–0.15 M, $I = 1.00$ M ($NaClO_4$), has been carried out.[174] The rate law (equation 36) indicates paths involving reaction with H_2O and OH^- ($k_1 = 0.33\ s^{-1}$, $k_{OH} = 2.22\ M^{-1}\ s^{-1}$ at 25 °C). The corresponding k_1 values for $[CrO_4]^{2-}$ ($3.2 \times 10^{-7}\ s^{-1}$) and $[WO_4]^{2-}$ ($0.44\ s^{-1}$) provide one of the few kinetic comparisons for Cr, Mo and W. The difference in rate constants is attributable to the larger enthalpy of activation in the case of chromate, reflecting tighter Cr^{VI}—O bonds. It has to be borne in mind that there are other contributing paths for chromate, the full rate law having been determined as equation (37). The molybdate exchange cannot readily be studied by ^{18}O labelling at pH 11, because protonation is effective and much faster rates are observed.[174]

$$\text{Rate} = k_1[MoO_4^{2-}] + k_{OH}[MoO_4^{2-}][OH^-] \tag{36}$$

$$\text{Rate} = k_1[CrO_4^{2-}] + k_2[HCrO_4^-] + k_3[H^+][HCrO_4^-] + k_4[HCrO_4^-] + k_5[HCrO_4^-]^2 \tag{37}$$

Fast monomer–dimer equilibria involving Mo^{VI} in 0.2–0.3 M $HClO_4$, $I = 3.0$ M ($LiClO_4$), have been studied by the temperature-jump method.[176] A major pathway involves rapid dimerization of a monomer form, referred to as $[HMoO_3]^+$, which might alternatively be written $[MoO_2(OH)(H_2O)_3]^+$ or a related form. At 25 °C, $I = 3.0$ M $[LiClO_4]$, rate constants are $k_f = 1.71 \times 10^5\ M^{-1}\ s^{-1}$, and $k_b = 3.2 \times 10^3\ s^{-1}$. Information has been obtained by the stopped-flow method for the interconversion of tetrahedral chromate and dichromate ions.[177] At pH 2–4 hydrogen chromate, $[HCrO_4]^-$, is specified as the reactant. From this and other similar studies on the substitution reactions of $[HCrO_4]^-$ there is evidence for a dissociative process.[178] Further information concerning precise formulae of Mo^{VI} in acidic solutions is required to enable more extensive comparisons.

Temperature-jump studies of Mo^{VI} solutions at pH 5.50–6.75 have been reported for the monomer–heptamer and heptamer–octamer interconversions which are complete within a few milliseconds.[179] Molybdate as $[HMoO_4]^-$ (here assumed to be tetrahedral) reacts with bidentate 8-hydroxyquinoline[180] and catechol,[181] to give octahedral products in net 4→6 conversions.[180] Table 4 summarizes the kinetic data, where different degrees of protonation of the ligating groups are indicated. For the reaction with edta a path assigned to the reaction of $[H_2edta]^{2-}$ with $[HMoO_4]^-$ gives a rate constant of $2.3 \times 10^5\ M^{-1}\ s^{-1}$.[182] A reaction in which the tetrahedral geometry of $[MoO_4]^{2-}$ is retained is the rapid stopped-flow equilibration of molybdate with $[Co(NH_3)_5(H_2O)]^{3+}$ (pK_a 6.3) at pH 7–8 (equation 38).[183]

$$[Co(NH_3)_5(H_2O)]^{3+} + [MoO_4]^{2-} \rightleftharpoons [Co(NH_3)_5(OMoO_3)]^+ + H_2O \tag{38}$$

Substitution is at the Mo^{VI} centre with retention of the Co—O bond. The first-order $[H^+]$-dependent term is consistent with $[HMoO_4]^-$ as a reactant, and the $[H^+]$-independent term is assigned to the reaction of $[HMoO_4]^-$ with $[Co(NH_3)_5OH]^{2+}$. An interesting situation arises in the reaction of $[MoO_4]^{2-}$ with $[Cr(edta)(H_2O)]^-$ at pH 7.3–8.7.[184] As in the case of

Table 4 Second-order Rate Constants for Reactions of $[HMoO_4]^-$ at 25 °C

Ligand	*Ionic strength*	*Coordination change at Mo^{VI}*	k ($M^{-1}\,s^{-1}$)
H-oxine	0.20	$4 \rightarrow 6$	4.5×10^6
H-oxine-SO_3^-	0.20	$4 \rightarrow 6$	3.9×10^6
oxine$^-$	0.20	$4 \rightarrow 6$	1.5×10^8
oxine-SO_3^{2-}	0.20	$4 \rightarrow 6$	4.0×10^7
H-catechol$^-$	0.10	$4 \rightarrow 6$	1.9×10^8
H_2-edta	0.10	$4 \rightarrow 6$	2.3×10^5
$[Co(NH_3)_5H_2O]^{3+}$	1.0	$4 \rightarrow 4$	3.2×10^5
$[Co(NH_3)_5OH]^{2+}$	1.0	$4 \rightarrow 4$	6.6×10^4
$[Cr(edta)H_2O]^-$	1.0	$4 \rightarrow 4$	3.1×10^4
HS^-	0.50	$4 \rightarrow 4$	1.3×10^6

H-oxine = 8-hydroxyquinoline.
H-oxine-SO_3^- = 8-hydroxyquinoline-5-sulfonic acid.
H-catechol$^-$ = product of first acid dissociation of catechol.

$[Co(NH_3)_5(H_2O)]^{3+}$, there are two terms for complex formation in the rate law, one of which can be assigned to the reaction of $[Cr(edta)(H_2O)]^-$ with $[MoO_4]^{2-}$ (rate constant 21 $M^{-1}\,s^{-1}$). The second, which is first order in $[H^+]$, corresponds to replacement of the H_2O of $[Cr(edta)H_2O]^-$ by $[HMoO_4]^-$ ($3.1 \times 10^4\,M^{-1}\,s^{-1}$). Whereas the first is believed to correspond to replacement of the H_2O (labilized by the presence of the carboxylate) at the Cr^{III}, the latter as in other cases corresponds to substitution at the Mo^{VI} centre. There are proton ambiguities however because the first reaction could also be assigned to the reaction of $[Cr(edta)OH]^{2-}$ (pK_a 7.4) with $[HMoO_4]^-$. In all these examples the interpretation requires that there are pathways in which there is protonation of $[MoO_4]^{2-}$ prior to complexation. Protonation labilizes at least one oxo ligand and may itself induce a $4 \rightarrow 6$ change in coordination to give a more labile species. Consistent with this, rates are much more rapid than for $H_2{}^{18}O$ exchange with $[MoO_4]^{2-}$.

Tetrahedral sulfido or thiolate complexes are known for a number of d^0 transition metal ions including Mo^{VI}.[185] Preparative procedures involve the reaction of solutions of oxyanions with H_2S. In addition to $[MoS_4]^{2-}$ the mixed oxo/sulfido complexes $[MoOS_3]^{2-}$, $[MoO_2S_2]^{2-}$ and $[MoO_3S]^{2-}$ are well characterized. Although the latter is difficult to obtain in a pure crystalline state, X-ray crystal structure information on $(NH_4)_2[MoS_4]$ (Mo—S = 2.17 Å),[186] and $Cs_2[MoOS_3]$ (Mo—S = 2.18 Å; Mo—O = 1.79 Å)[187] have been reported, and the Mo—O distance is slightly longer than in Mo^{VI} complexes $K_2[MoO_4]$ (1.76 Å), $[MoO_3(dien)]$ (1.74 Å) and $[Mo_2O_5(C_2O_4)_2(H_2O)_2]^{2-}$ (Mo—O$_t$ 1.69 Å). Bridged Mo^{VI} μ-sulfido complexes do not appear to be formed and there are no counterparts in the polymeric (and heteropoly) species found from $[MoO_4]^{2-}$. Kinetic studies on the interconversion of $[MoO_xS_{4-x}]^{2-}$ forms have been carried out.[188] The 1:1 equilibration of H_2S with $[MoO_4]^{2-}$ can be expressed as in equation (39).

$$[MoO_4]^{2-} + H^+ + HS^- \underset{k_{10}}{\overset{k_{01}}{\rightleftharpoons}} [MoO_3S]^{2-} + H_2O \qquad (39)$$

There are few quantitative studies with H_2S as a reactant, and some difficulties were experienced in choosing conditions appropriate to the study. At pH 9.2–10.2 (0.25 M NH_3/NH_4^+ buffer), $I = 0.50$ M (NaCl), plots of equilibration rate constants k_{eq} against $[MoO_4^{2-}]$ are in accord with equation (40).

$$k_{eq} = k_f[MoO_4^{2-}] + k_b \qquad (40)$$

The formation constant k_f is dependent on $[H^+]$ giving $k = 4.0 \times 10^9\,M^{-2}\,s^{-1}$, and k_b for the reverse reaction is $6.5 \times 10^{-3}\,s^{-1}$. Interpretation of k in terms of a reaction between $[HMoO_4]^-$ and HS^- is preferred rather than the alternative of $[MoO_4]^{2-}$ with H_2S, and on this basis a second-order rate constant of $1.3 \times 10^6\,M^{-1}\,s^{-1}$ is obtained, of similar magnitude to those listed in Table 4. Other formation rate constants for the different $[MoO_xS_{4-x}]^{2-}$ ions have to be given in the form of the experimental third-order rate constants since the relevant protonation constants are not known. For the rate law $k[MoO_xS_{4-x}^{2-}][HS^-][H^+]$, k values range from $4.0 \times 10^9\,M^{-2}\,s^{-1}$ for the reaction of $[MoO_4]^{2-}$ to less than $1.6 \times 10^6\,M^{-2}\,s^{-1}$ for $[MoOS_3]^{2-}$. Rate constants for aquation of $[MoO_3S]^{2-}$ ($6.5 \times 10^{-3}\,s^{-1}$), $[MoOS_3]^{2-}$ ($\sim 5 \times 10^{-5}\,s^{-1}$) and

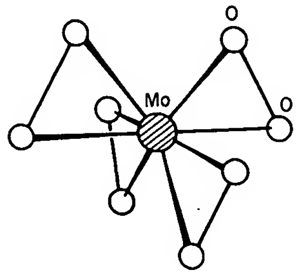

Figure 35 The structure of the Mo^{VI} peroxo complex, $[Mo(O_2)_4]^{2-}$ [190]

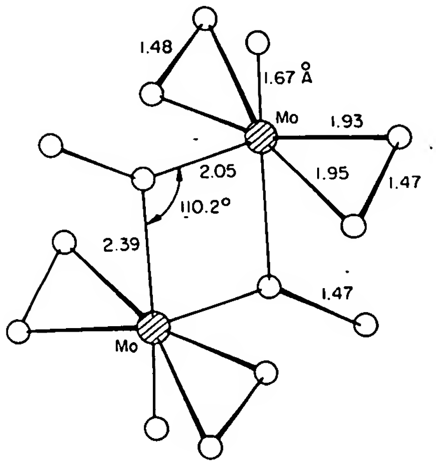

Figure 36 The structure of the Mo^{VI} peroxo/hydroperoxo complex $[(O_2)_2OMo(OOH)_2MoO(O_2)_2]^{2-}$ [196]

$MoS_4]^{2-}$ ($1.6 \times 10^{-6}\,s^{-1}$) indicate a trend to smaller values as more sulfide ligands are ntroduced. The presence of sulfide does not appear to give a labilizing effect.

Different crystalline phases can be separated from aqueous solutions of potassium nolybdate(VI) following reaction with varying amounts of hydrogen peroxide, pH 4–8.[189] Crystal structure determinations of $[Zn(NH_3)_4][Mo(O_2)_4]$,[190] $K_2[O\{MoO(O_2)_2(H_2O)\}_2]\cdot 2H_2O$,[190] $K_4[Mo_4O_{12}(O_2)_2]$[192] and $K_6[Mo_7O_{22}(O_2)_2]\cdot 8H_2O$[193] have for example been reported. In all cases the O_2^{2-} is bound sideways to the metal, with O—O distances varying from 1.38 to 1.55 Å, but generally around 1.48 Å, which is the expected value for peroxide. The peroxo ligands in the dark red $[Mo(O_2)_4]^{2-}$ compound (O—O distance 1.55 Å) are positioned tetrahedrally about the Mo^{VI} (Figure 35). A Cr^{V} analogue $[Cr(O_2)_4]^{3-}$, having a similar configuration (O—O distance 1.48 Å), is known. An interesting variation is the occurrence of hydroperoxide as a bridging ligand in $(pyH)_2[(O_2)_2OMo(OOH)_2MoO(O_2)_2]$,[194] where the bridge has a pendant —O(OH)— arrangement (Figure 36). Only one other example of this structure is known in the Co_2^{III} complex $[(en)_2Co(NH_2, O_2H)Co(en)_2]^{4+}$.[195] The complex $K_2[MoO(O_2)_2(C_2O_4)]$ is monomeric,[196] and to be regarded as five- or seven-coordinate depending whether the O_2^{2-} is assigned one or two coordination positions.

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